7-NORBORNADIENYLIDENE

By

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1978

To my parents

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT	ix
INTRODUCTION	1
RESULTS AND DISCUSSION	19
EXPERIMENTAL	61
General.	61
7-t-Butoxynorbornadiene (67).	61
7-Chloronorbornadiene (50).	62
Silver Isocyanate (71).	62
7-Norbornadienylisocyanate (68).	63
Methyl N-7-Norbornadienylcarbamate (69).	64
p-Chlorobenzoyl Nitrite (73).	65
Methyl N-Nitroso-N-7-norbornadienylcarbamate (64).	65
Bases Used in the Attempts to Generate 7-Norbornadienylidene (1) from Methyl N-Nitroso-N-7-norbornadienylcarbamate (64) and N-Nitroso-N-7-norbornadienylurea (65).	66
Decomposition of Methyl N-Nitroso-N-7-norbornadienylcarbamate (64) by Sodium Methoxide.	68
Decomposition of Methyl N-Nitroso-N-7-norbornadienylcarbamate (64) by Lithium Ethoxide.	69
7-Norbornadienylurea (70).	70

Page

N-Nitroso-N-7-norbornadienylurea (65). 71

Typical Decomposition of N-Nitroso-N-7-norborna-dienylurea (65) under Basic Conditions. 72

Decomposition of N-Nitroso-N-7-norbornadienylurea (65) in Heptane at 90°. 72

Decomposition of N-Nitroso-N-7-norbornadienylurea (65) in Heptane in the Presence of Dimethylfumarate at 90°. 73

Decomposition of N-Nitroso-N-7-norbornadienylurea (65) in Heptane in the Presence of Lithium Carbonate at 90°. 74

Decomposition of N-Nitroso-N-7-norbornadienylurea (65) in Triglyme at 200°. 75

Experimental Method for Thermolysis of N-Nitroso-N-7-norbornadienylurea (65) in a Hot Tube. 75

Typical Thermolysis of N-Nitroso-N-7-norbornadienyl-urea (65) in a Hot Tube at 300°. 78

Typical Thermolysis of N-Nitroso-N-7-norbornadienyl-urea (65) in a Hot Tube at 400°. 78

Thermolysis of N-Nitroso-N-7-norbornadienylurea (65) in a Hot Tube at 400° and Trapping with Tetra-cyanoethylene (TCNE). 80

Sodium Salt of Benzaldehyde Tosylhydrazone. 81

Thermolysis of the Sodium Salt of Benzaldehyde Tosylhydrazone (113) in a Hot Tube at 400°. 81

Heptafulvalene (14). 81

Thermolysis of Heptafulvalene (14) in a Hot Tube at 400°. 81

Isolation and Identification of syn- and anti-Penta-cyclo[$10.2.0.0^{4,12}.0^{5,11}.0^{8,11}$]tetradeca-2,6,9,13-tetraene (18) and (19). 82

Thermolysis of syn- and anti-Pentacyclo [$10.2.0.0^{4,12}.0^{5,11}.0^{8,11}$]tetradeca-2,6,9,13-tetraene (18) and (19) in a Hot Tube at 350°. 82

Page

APPENDIX 84

REFERENCES AND NOTES 94

BIOGRAPHICAL SKETCH 99

LIST OF TABLES

Page

Table 1. Decomposition of N-Nitroso-N-7-norbornadienylurea (65) Under Basic Conditions. 72

Table 2. Thermolysis of N-Nitroso-N-7-norbornadienylurea (65) in a Hot Tube. 80

LIST OF FIGURES

Page

Figure 1 36

Figure 2 37

Figure 3 38

Figure 4 39

Figure 5 40

Figure 6 41

Figure 7 42

Figure 8 76

Figure 9 83

Abstract of Dissertation Presented to the
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7-NORBORNADIENYLIDENE

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Chairman: William M. Jones
Major Department: Chemistry

7-Norbornadienylidene (1) has been particularly resistant to generation in the past. Not only would it fill an important gap in the present knowledge of the C_7H_6 energy surface but it would also be the premier example of a group of carbenes known as foiled methylenes. A systematic study has been carried out using methyl N-nitroso-N-7-norbornadienylcarbamate (64) and N-nitroso-N-7-norbornadienylurea (65) as potential precursors for (1). Both (64) and (65) were prepared by treating the corresponding unnitrosated material with p-chlorobenzoyl nitrite (PCBN) (73) at -45° in ether. Treatment of (64) and (65) with various bases in a variety of solvents and under a number of conditions gave no evidence for any carbene products. Pyrolysis of (65) in heptane at 90° and in triglyme at 200° gave no products which could be linked to (1).

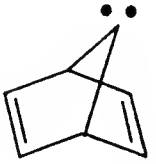
When the normal method of flash vacuum thermolysis was used on (65), no useful results were obtained owing to the relatively low volatility of (65). However, when (65) was pyrolyzed by dropping it down a heated inclined tube which was being continuously evacuated and the products condensed in a liquid nitrogen trap, the following results were obtained: from 200 to 300° a mixture of syn- and anti-pentacyclo[10.2.0.0^{4,12}.0^{5,11}.0^{8,11}]tetradeca-2,6,9,13-tetraene (18) and (19) respectively was obtained in yields averaging 14%, from 250 to 350° heptafulvalene (14) in yields averaging 15%, from 200 to 400° benzene (22) in yields of about 3%, and toluene (23) at 200 and 250° in a 4% yield. In one experiment at 400° the volatile products were allowed to react with tetracyanoethylene (TCNE). Nuclear magnetic resonance analysis of the products showed weak signals corresponding to those published in the literature for 5,5,6,6-tetracyano-7-vinylidenebicyclo[2.2.1]hept-2-ene (114). Thus the presence of fulveneallene (12) was strongly suggested.

These results suggest an attractive mechanism. Pyrolysis of (65) results in the generation of (1) which then either fragments to give (22) and a carbon atom or rearranges to bicyclo[3.2.0]hepta-1,3,6-triene (6). The bicyclic triene (6) then, depending on the temperature, dimerizes to give the mixture of isomeric dimers (18) and (19), rearranges to cycloheptatrienylidene (3) which then dimerizes to give the observed (14), or (6) rearranges to (12). Three alternative

mechanisms, one involving phenylcarbene (2) as the progenitor of (14); another involving dimerization of (1) to give binorbornadienylidene (26) and subsequent rearrangement of (26) to (14), (18), and (19); and another involving generation of bicyclo[2.2.1]hepta-1,2,5-triene (123) and subsequent rearrangement to 4-bicyclo-[3.2.0]hepta-2,6-dienylidene (124) followed by rearrangement of (124) to (6); cannot be entirely discounted.

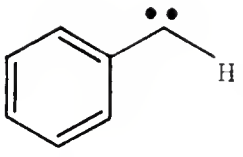
INTRODUCTION

7-Norbornadienylidene (1) has been in the past particularly resistant to generation. Either the popular methods for generation of carbenes simply did not work or the precursors needed for the method were not synthetically available.[1-3] This left a significant void and was quite discouraging since (1) remained as one of the last species on the C_7H_6 energy surface to be generated which was chemically reasonable.



(1)

For some time now interest has been high in the various isomers which comprise the C_7H_6 energy hypersurface.[4-27] The isomers which have been generated or implicated to date are shown below. A considerable amount of energy has been expended by various research groups in determining the relationships between these isomers. For example, generation of phenylcarbene (2) from various precursors in the gas phase led at temperatures below 580^{o} to heptafulvalene



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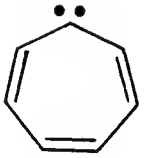

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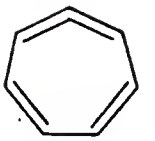

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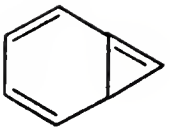

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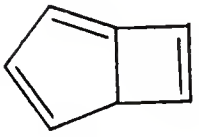

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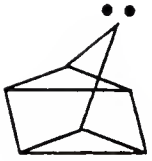

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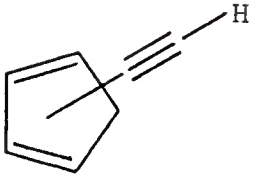

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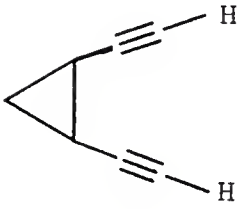

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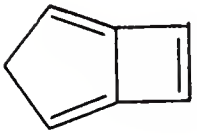

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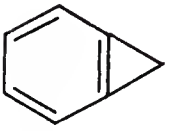

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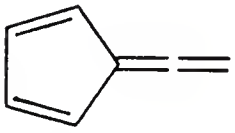

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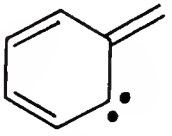
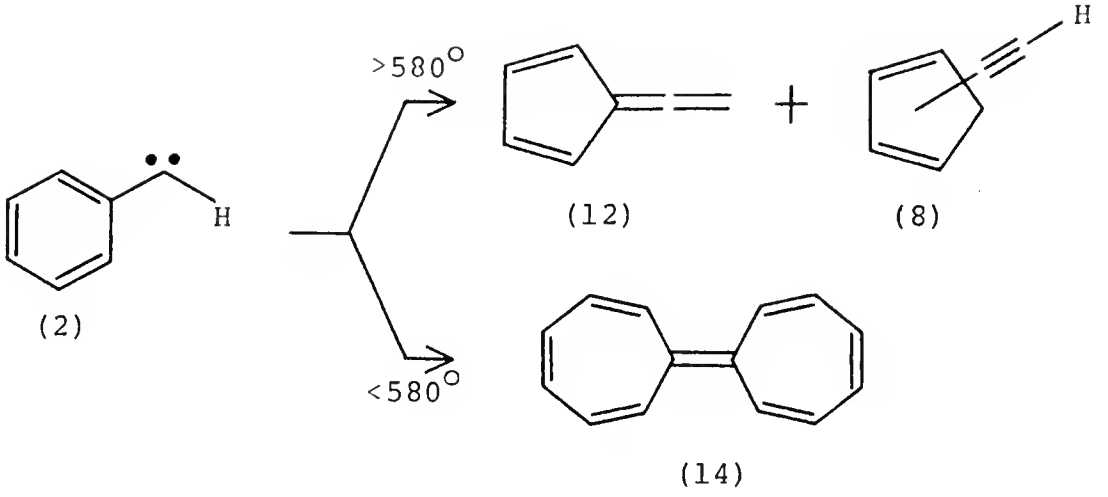


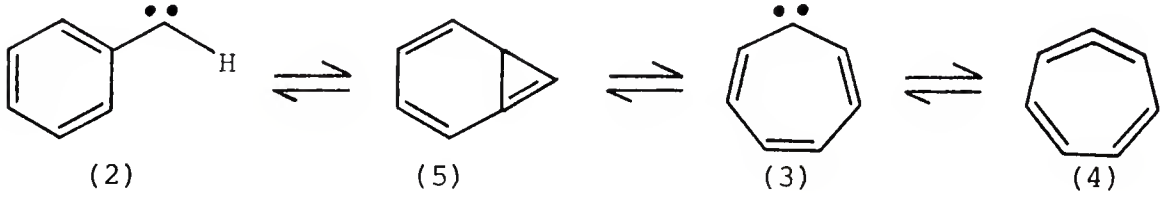
(13)

(14), a ring expansion product.[4,5] At temperatures above 580° fulveneallene (12) and ethynylcyclopentadiene (8), both ring contraction, products were formed.[5,6]

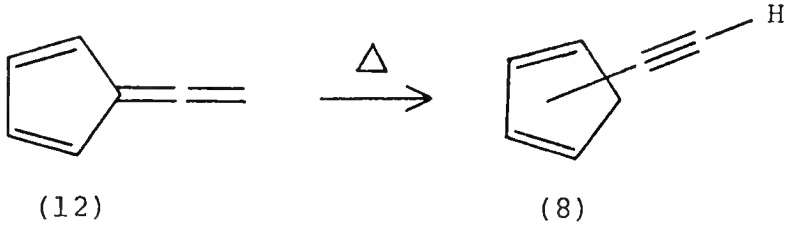
As regards the ring expansion the equilibria, which may exist between the four species shown below have received considerable attention.[12,14,18-20,22,23] There is little doubt as to the intermediacy of bicyclo[4.1.0]hepta-2,4,6-triene (5).[22] However, the identity of the intermediate which leads to (14) whether it be cycloheptatrienylidene (3)



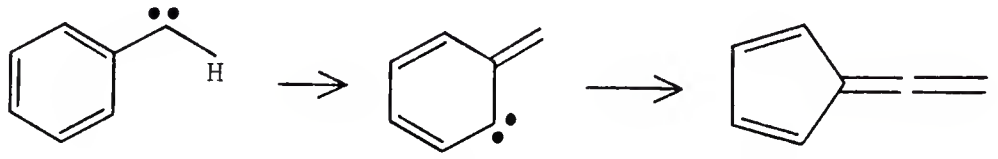
and/or cycloheptatetraene (4) is still being investigated.



In the ring contraction ethynylcyclopentadiene (8) has been shown to be a secondary product of fulveneallene (12) whenever fulveneallene (12) is exposed to higher temperatures.[20] Several mechanisms have been presented by workers

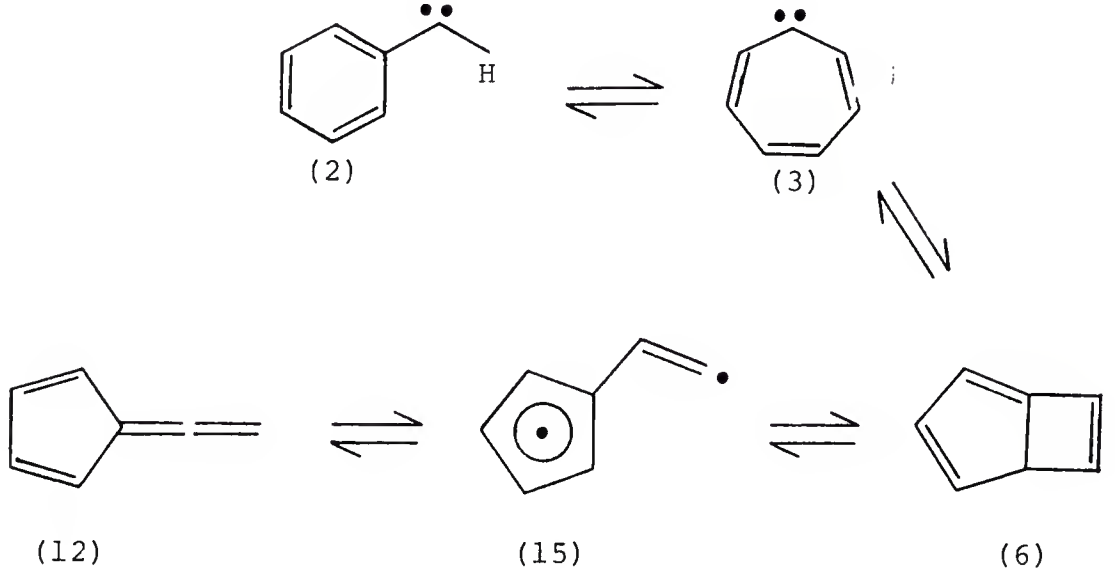


through the years to explain the ring contraction.[6,14,20,24] One of these, first proposed by Wiersum and Hageman,[24] involved rearrangement of (2) to methylenecyclohexadienylidene (13) which then rearranged to (12). Recently, however, evidence based



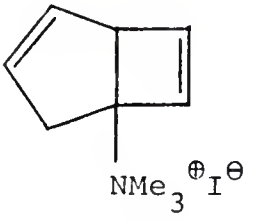
(2) (13) (12)

on ^{13}C labeling studies has been presented by C. Wentrup and coworkers which discounts this and other previously suggested mechanisms and favors one in which ring expansion occurs and then is followed by rearrangement of (3) to bicyclo-[3.2.0]hept-1,3,6-triene (6) at high temperature.[21] The bicyclic triene (6) then gives (12) presumably via the free radical (15).



(2) (3) (12) (15) (6)

The bicyclic triene (6) has been generated independently by two groups of workers.[25-27] Hoffman elimination of (16)[26] and dehydrohalogenation of (17)[25] both led to (6). However, the monomer (6) could in no case be isolated. Instead a pair of isomeric dimers, syn- and anti-pentacyclo-[10.2.0.0^{4,12}.0^{5,11}.0^{8,11}]tetradeca-2,6,9,13-tetraene (18) and (19) respectively, was obtained. Presumably these were a result of 2 + 2 cycloaddition across the 1,2 double bond of (6).[26]



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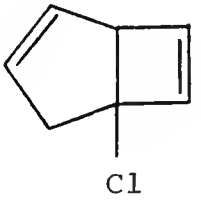

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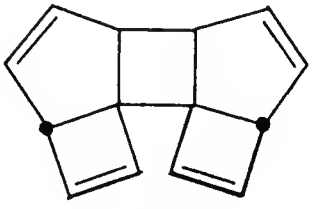

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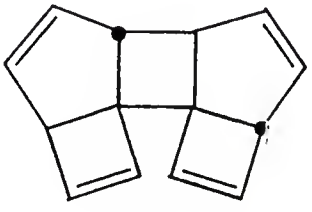
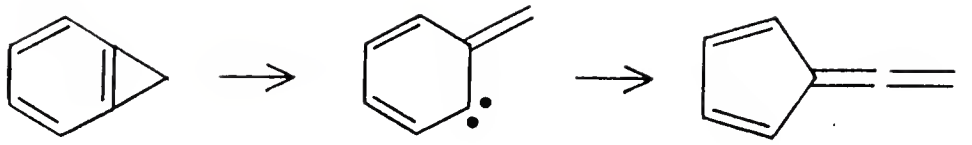


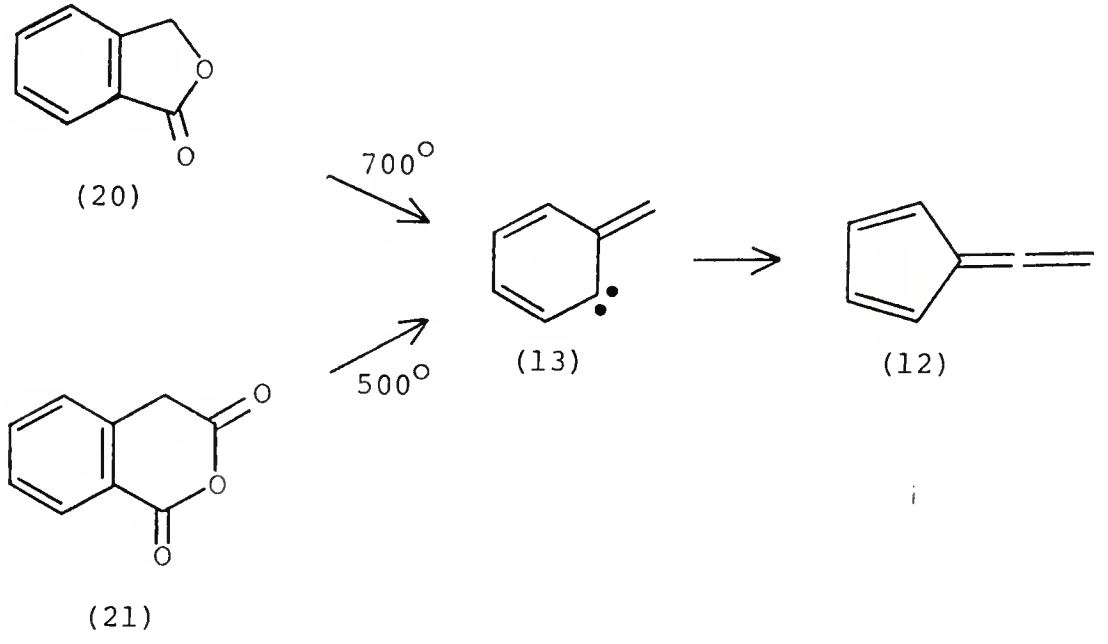
(19)

Pyrolysis of benzocyclopropene (11) at 500^{o} gives (12).[17] The cyclopropyl ring of (11) breaks to give (13) which then rearranges to (12). Other precursors to (13) also give (12) upon gas phase thermolysis.[11,15]



(11) (13) (12)

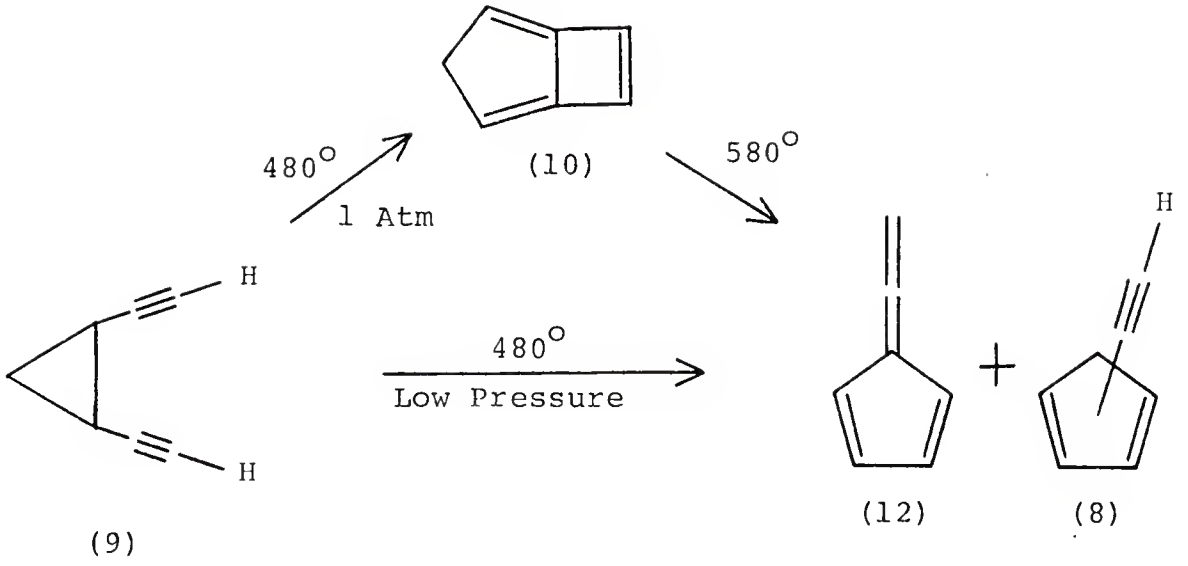
Bergman found that gas phase flow thermolysis of 1,2-diethynylcyclopropane (9) at 480° and 1 atmosphere gave bicyclo[3.2.0]hepta-1,4,6-triene (10).[16] When (10) was generated at a low pressure or when (10) was heated at 580°,



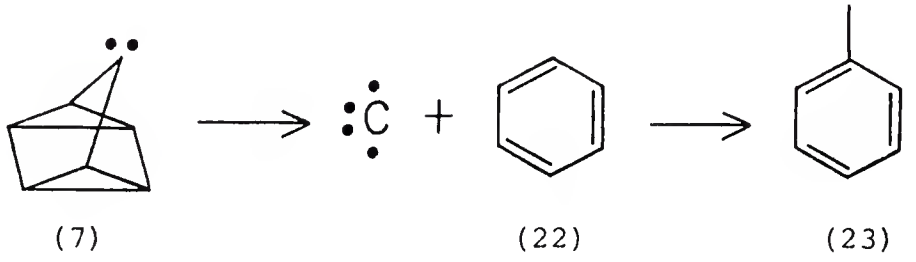
(20) (13) (12)

(21)

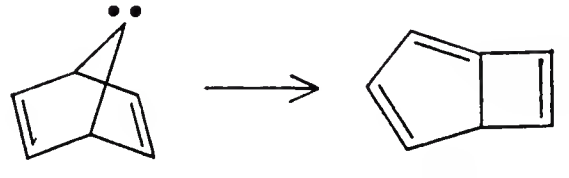
(12) and (8) were produced. Wolf and Shevlin generated quadricyclanylidene (7) and found that it extrudes its C-7

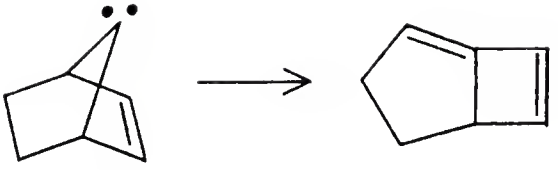


carbon atom to give benzene (22) and toluene (23) as products.[8]



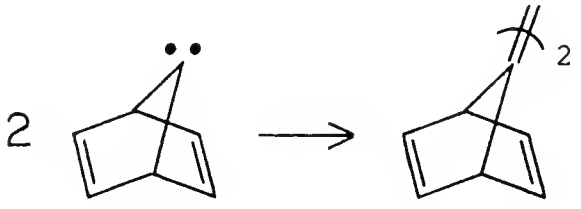
In the case of 7-norbornadienylidene (1) a number of possibilities come to mind. For instance, (1) could rearrange by what is formally a 1,2 shift to give (6). Moss et al. have found that 7-norbornenylidene (24) rearranges to bicyclo[3.2.0]hepta-1,6-diene (25).[28] Another possible





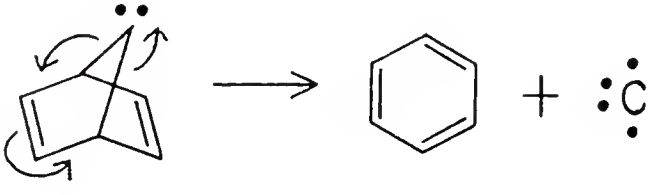
(24) (25)

fate is that (1) could simply dimerize to give binorbornadienylidene (26). Another possibility would be loss of



(1) (26)

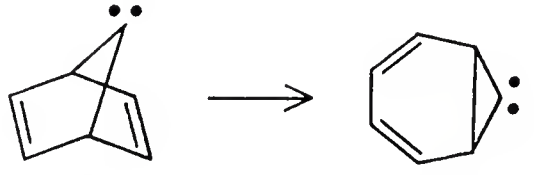
the carbene bridge to give benzene (22) and a carbon atom. This would of course correspond to the behavior found for quadricyclanylidene (7).[8] While on the subject of (7) it is conceivable that (1) might isomerize to (7). However, this is unlikely because from simple thermochemical



(1) (22)

(1) (7)

considerations (7) is calculated to be 40 kcal/mole higher energy than (1). Finally, (1) could undergo what might be called a retro-Skattebøl[22] rearrangement to give the unknown carbene norcaradienylidene (27). However, this type of rearrangement is without precedent and is only known to take place in the opposite sense as in the case of the rearrangement of vinylcyclopropylidenes to cyclopentenylidenes.[22]

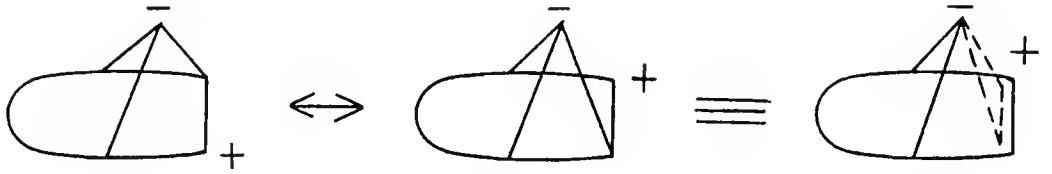


(1) (27)

In addition to the significance of (1) as a C_7H_6 isomer it remained as the premier example of a group of carbenes known as foiled methylenes or nonclassical carbenes.[28-43] By definition "these are systems in which an artificial energy minimum is created as a result of initial stabiliza-

tion due to the inception of a typical facile methylene reaction, such as addition to a double bond, which is foiled by the impossibility of attaining the final product geometry."[29, p. 5458] This can be viewed in a general way as shown below. In (28) the carbene cannot add to the double bond

(28) (29)

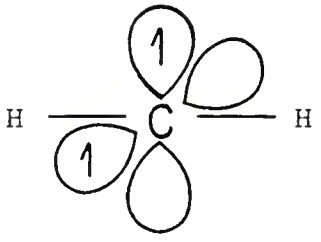


(30) (31) (32)

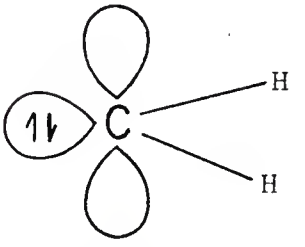
because of the impossible geometry that would result. However, the carbene center could interact with the double bond and one can draw two resonance structures which together result in the nonclassical structure (32). In principle then, such an interaction would have a stabilizing influence on the molecule.

Interest in these types of carbenes has been particularly high since Gleiter and Hoffman stated in 1968 that foiled methylenes may be a way to obtain a carbene with a singlet ground state.[29] The structures for singlet and triplet

carbenes are shown below. Gleiter and Hoffman stated that

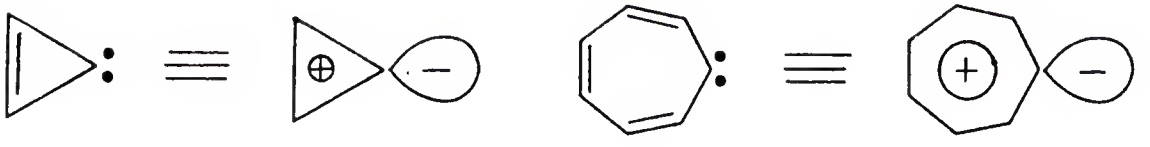


Triplet
sp Hyberdized



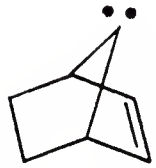
Singlet
sp^2 Hyberdized

in order to obtain a singlet ground state the degeneracy of the triplet methylenes p_x and p_y orbitals would have to be destroyed and that one way to accomplish this would be to force one of the p orbitals to interact with a high lying occupied level.[29] In principle this would be the case with a foiled methylene. In addition it is clear from structures (30), (31), and (32) that the carbene center may have taken on increased neucleophilic character. In this way (1) may be similar to cyclopropenylidene (33) and cycloheptatrienylidene (3).[29]

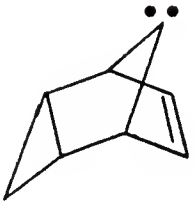


(33) (3)

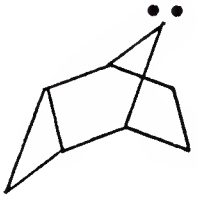
A considerable amount of work has been done by various research groups to date on foiled methylenes.[28-43] The particular ones that have been studied so far are shown below.



(24)



(34)



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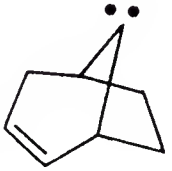

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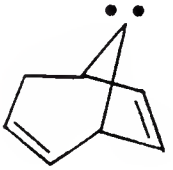

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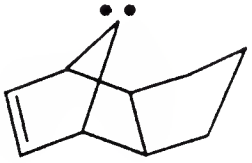

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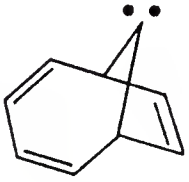

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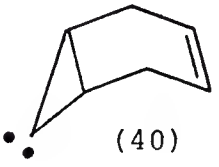
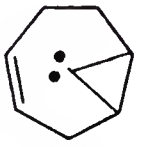


(40)



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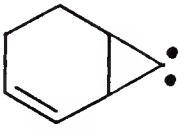
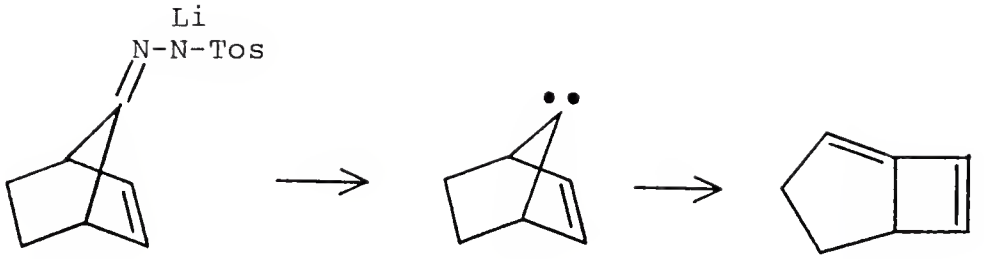


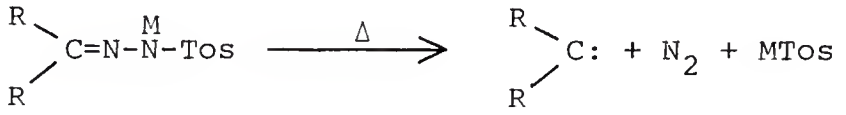
(42)

A detailed review of this chemistry will not be attempted here. However, Moss and others have generated 7-norbornenylidene (24) and studied its behavior in detail.[28,40-42] Moss et al. have found that a mixture of products was formed when they pyrolyzed the lithium salt of 7-norbornenone tosylhydrazone (43) at 190° with the major product being the bicyclic diene (25).[28] The chemistry of the other foiled methylenes has been similar; that is, products have been formed which suggest interaction between the carbene and the double bonds. Nevertheless, these products can all be explained by a simple 1,2 shift not involving any kind of nonclassical structure. To this date no definitive evidence for either case has been obtained.

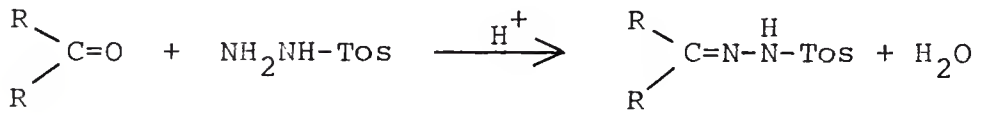


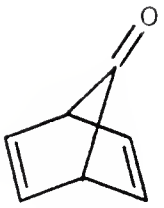
(43) (24) (25)

Attempts to generate 7-norbornadienylidene (1) by using the popular methods for the generation of carbenes failed.[1-3] These attempts centered on the Bamford-Stevens reaction[44] and α-elimination of hydrohalides.[45] In the case of the Bamford-Stevens reaction which involves the thermolysis of alkali metal salts of tosylhydrazones the problem centered around preparation of the tosylhydrazone itself.[1] Tosylhydrazones

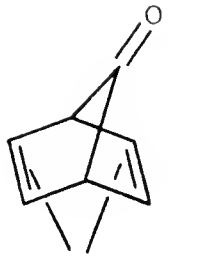


are normally prepared from the corresponding ketone and tosylhydrazide. However, (44) is inherently unstable.[46]



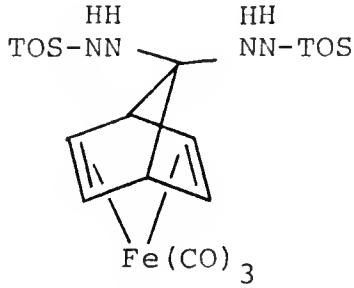


(44)



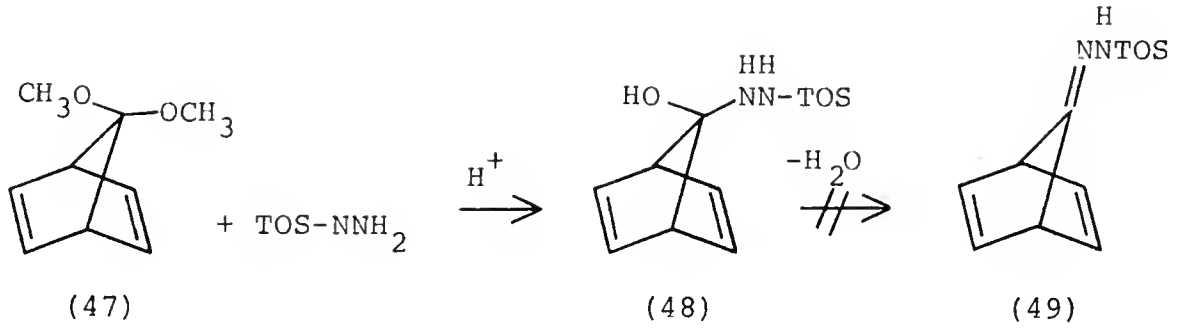
(45)

Preparation of the iron tricarbonyl complex of 7-norbornadiene (45) may have opened the door; however, attempts to prepare the tosylhydrazone led only to the ketal type material (46).[1] Jones and Ledford attempted to prepare the tosylhydrazone



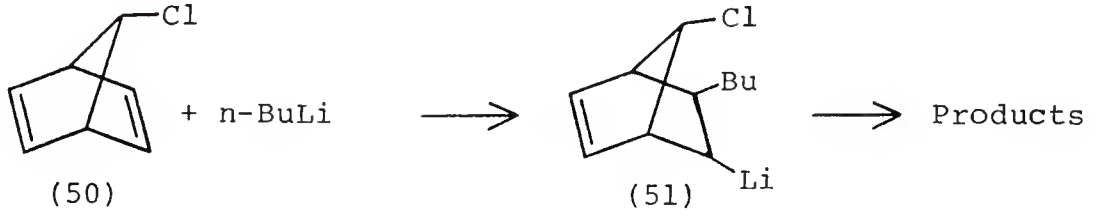
(46)

from 7,7-dimethoxynorbornadiene (47). Although this led to (48), it could not be dehydrated.[2] In the case of hydrohalide elimination, an attempt to generate (1) from



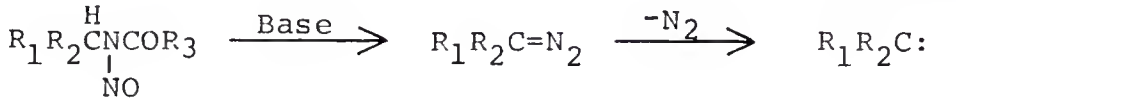
(47) (48) (49)

7-chloronorbornadiene (50) in the presence of n-butyl lithium led only to products derived from attack on the double bond by the base.[3]

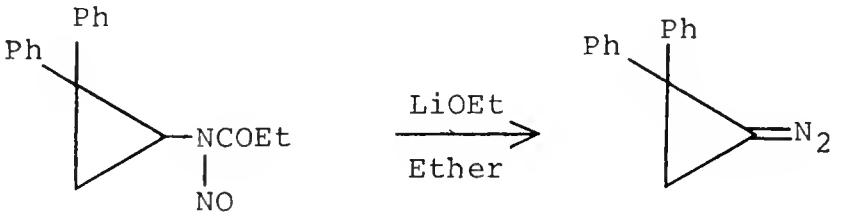


(50) (51)

Clearly, another type of precursor was called for if (1) was to be generated. For some time now a method used with success to generate carbenes has been the basic decomposition of N-nitroso amide derivatives.[47] As shown this involves production of the corresponding diazoalkane which then may lose nitrogen to give the carbene. For example,

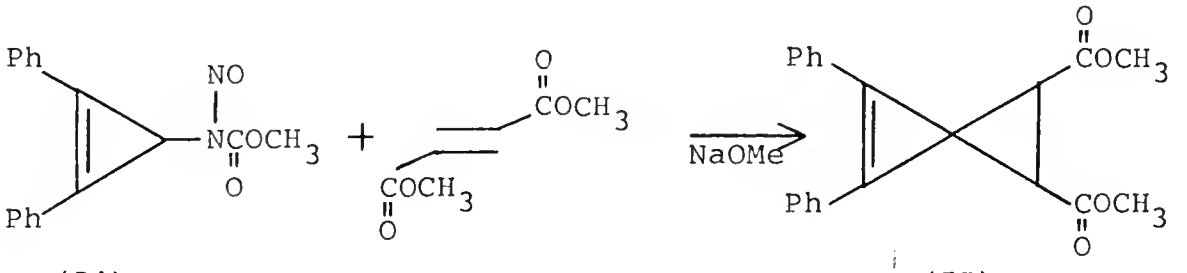


Jones and Muck discovered that treatment of (52) with lithium ethoxide in ether gave the diazoalkane (53).[48] In addition Jones and Warner found that treatment of (54) under



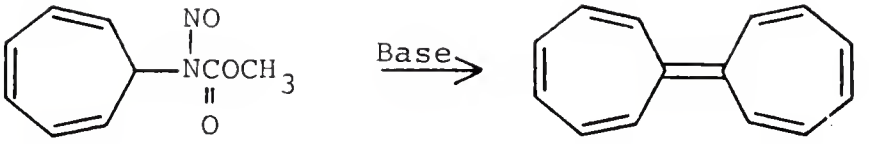
(52) (53)

carefully controlled conditions with sodium methoxide in the presence of dimethylfumarate gave up to 60% of the spiro adduct (55).[49] Moreover, decomposition of (56) with



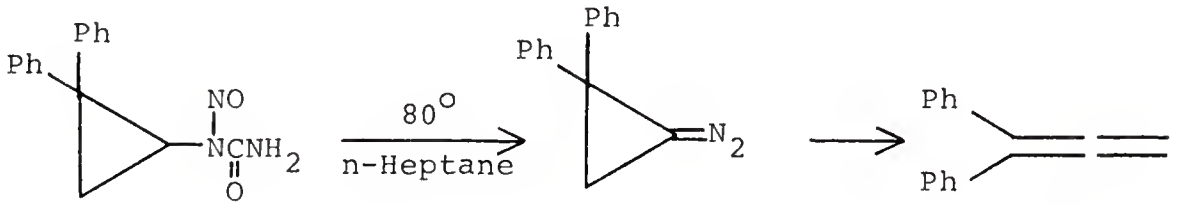
(54) (55)

base led to yields of up to 13% of (14).[50] In addition to the treatment of N-nitroso amide derivatives with bases to produce diazoalkanes, N-nitroso ureas have been thermolyzed and given diazoalkanes in a few instances. It was found that thermolysis of (57) in heptane at 80° gave up to 95%



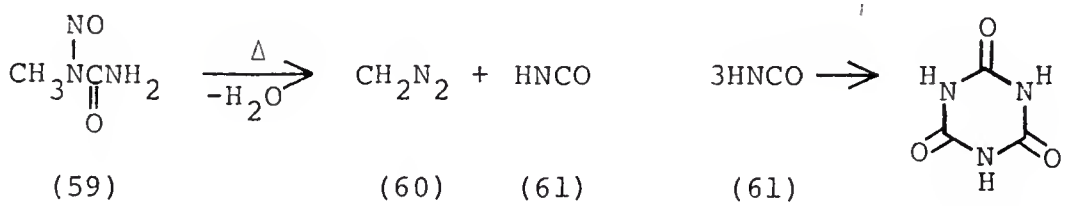
(56) (14)

of 1,1-diphenylallene (58).[51] Furthermore, the thermolysis

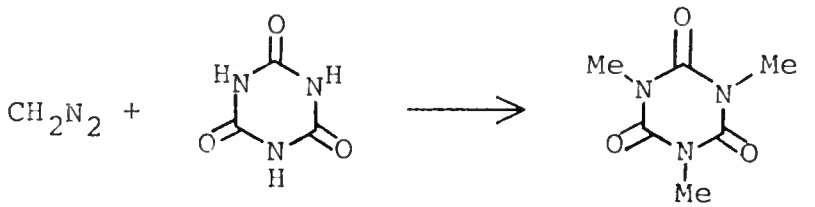


(57) (53) (58)

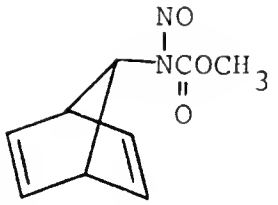
of N-nitroso-N-methylurea (59) gave diazomethane (60). However, in this case the carbene was not formed because (60) was trapped by cyanuric acid (62), formed as a by-product in the reaction, to give trimethyl isocyanurate (63).[52-54]



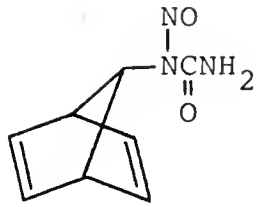
(59) (60) (61) (61) (62)



(60) (62) (63)



(64)



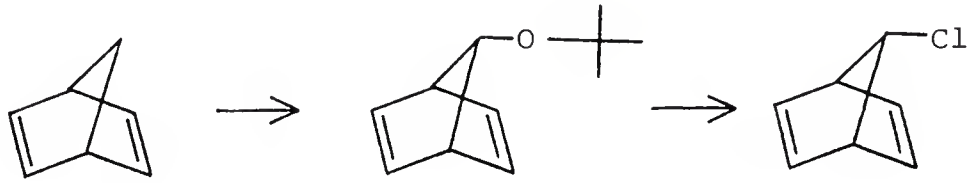
(65)

Therefore, two target molecules were picked, methyl N-nitroso-N-7-norbornadienylcarbamate (64) and N-nitroso-N-7-norbornadienylurea (65), to be synthesized which would be used to attempt to generate (1).

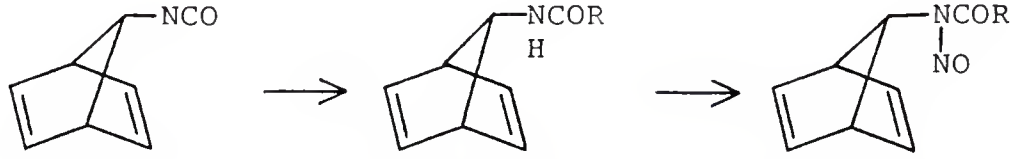
RESULTS AND DISCUSSION

The syntheses of the two potential precursors (64) and (65) were accomplished in five steps. The basic scheme without reagents and conditions is shown below.

Two of these steps, the conversion of 7-chloronorbornadiene (50) into 7-norbornadienylisocyanate (68) and especially conversion of methyl N-7-norbornadienylcarbamate (69) or 7-norbornadienylurea (70) into either (64) or (65) respectively, were rather problematic.



(66) (67) (50)

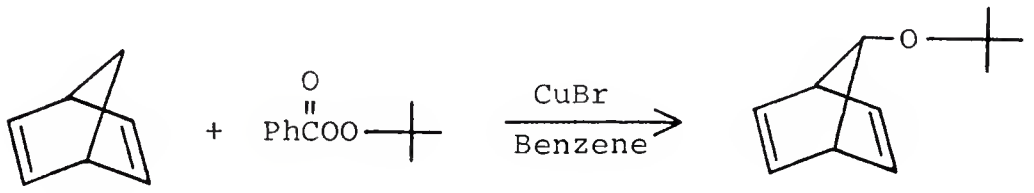


(68)

R=-OCH_3 (69)
R=-NH_2 (70)

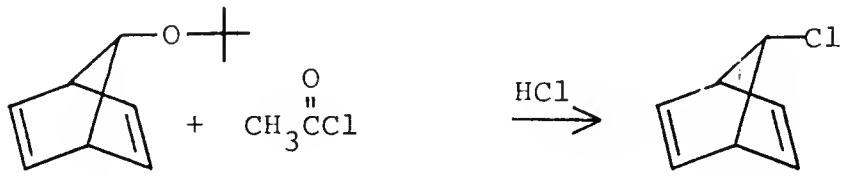
R=-OCH_3 (64)
R=-NH_2 (65)

7-t-Butoxynorbornadiene (67) was either used as obtained from Frinton Labs or it was prepared according to the method of Story and Fahrenholtz. This was an Organic Syntheses preparation and involved treatment of norbornadiene (66) with t-butyl perbenzoate in the presence of cuprous bromide.[55]



(66) (67)

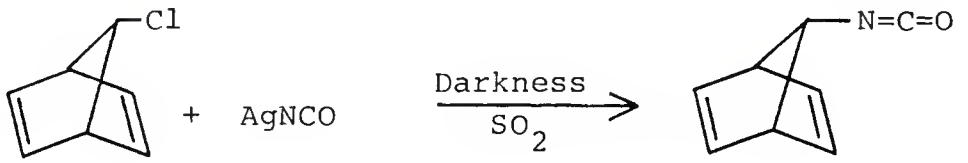
The chloride (50) was prepared by the method of Story and Saunders with minor modifications.[56] Treatment of the ether (67) with dry hydrogen chloride in refluxing acetyl chloride gave a satisfactory yield of the desired material (50).



(67) (50)

Preparation of the isocyanate (68), however, was somewhat more problematic. Although the following procedure was sound the yield reported was not obtained immediately. Synthesis of (68) was accomplished by treatment of the

chloride (50) with silver isocyanate (71) using refluxing liquid sulfur dioxide as the solvent. The reaction was carried out in darkness to protect (71) which is light sensitive. The isocyanate (68) was isolated in a 94% yield as an orange oil. Such a yield was not obtained in the early

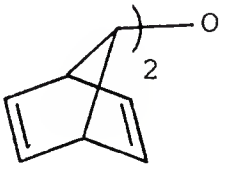


(50) (71) (68)

runs and low yields plagued the synthesis. Normally the isocyanate (68) was immediately used upon its preparation to make the carbamate (69) and the urea (70) since in a few cases polymerization of (68) had taken place. Because of this procedure the reason for the low yield was unclear. However, examination of the crude reaction mixture in one of the urea runs via its nmr spectrum showed another material besides the urea to be present in significant quantity. That this material had originated earlier in the reaction sequence was shown by examining the nmr spectrum of the isocyanate (68) used to prepare the urea. Indeed a material with identical spectral characteristics was a major proportion of the isocyanate mixture. This material was isolated by column chromatography and identified as 7-norbornadienylether (72). The spectral data were as follows: NMR ($CDCl_3$) τ 3.3-3.6 (m, 8H, olefinic),

5.5-5.7 (m, 2H, C-7), 6.3-6.5 (m, 4H, bridgehead); ir (neat) 1100, 1010 cm^{-1} on Beckman IR 10; ms m/e 198 (M+), 108, 107, 91 (base), 79, 78, 77, 65.

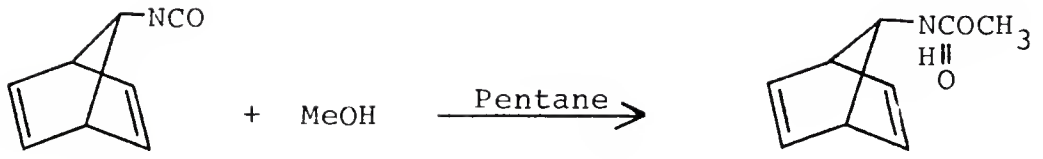
The silver isocyanate (71) that was being used was prepared in the laboratory by precipitating (71) from an aqueous solution of potassium cyanate with an aqueous solution of silver nitrate. However, a check of the literature uncovered the fact that (71) prepared from the above materials without proper pH control gives a product contaminated with silver oxide and silver carbonate.[57] When the method of Birkenbach and Linhard was substituted, the



(72)

pH of the potassium cyanate solution was brought to 6.2 with 1.0 M nitric acid before mixing with the silver nitrate solution, a product free of oxides and carbonates was obtained.[58] Use of this silver isocyanate (71) gave the high yield of (68) reported.

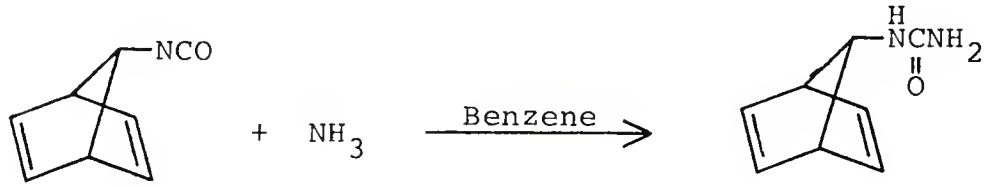
The carbamate (69) was prepared by stirring (68) at room temperature with methanol in pentane. This gave (69) as a white solid in a 19% yield based on starting chloride (50). The urea (70) was prepared by treating (68) with ammonia in benzene at room temperature. Recrystallization



(68) (69)

of crude (70) from hot tetrahydrofuran gave (70) as a beige solid in a 26% yield based on the isocyanate (68).

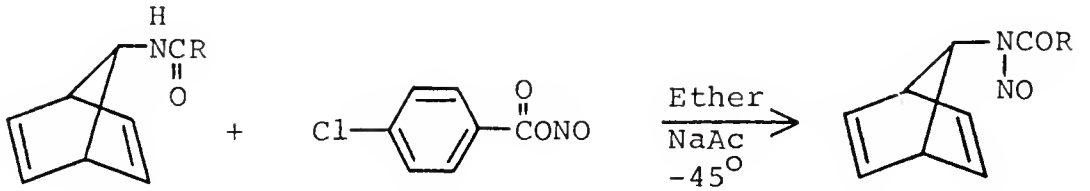
Synthesis of the two target molecules (64) and (65)



(68) (70)

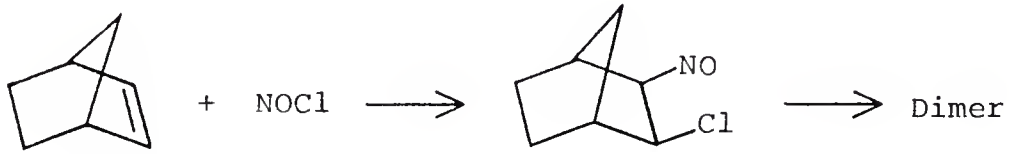
from either (69) or (70) respectively was accomplished after the correct nitrosating reagent was found. Treatment of (69) or (70) with p-chlorobenzoyl nitrite (PCBN) (73) in the presence of freshly fused anhydrous sodium acetate at -45° using anhydrous ether as a solvent gave (64) or (65) respectively. The N-nitrosocarbamate (64) was obtained as a yellow oil in 79% yield. The N-nitrosourea (65) was obtained as canary yellow needles in a 38% yield. It was initially felt that the most troublesome step in the synthesis would be this last step and that turned out to

be the case. Although the reaction worked quite well as

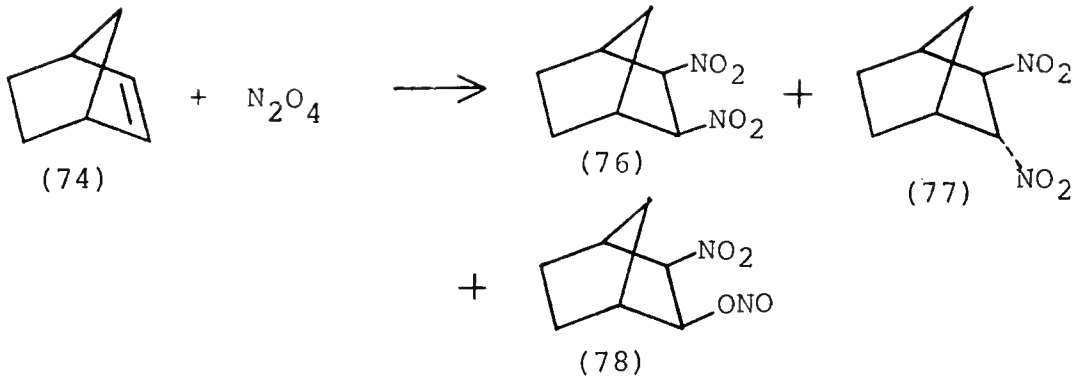


R=-OCH_3	(69)	(73)	R=-OCH_3 (64)
R=-NH_2	(70)		R=-NH_2 (65)

reported above, this was not the case until the correct nitrosating reagent was found. The traditional reagents for nitrosating amide derivatives have been sodium nitrite and hydrochloric acid, nitrosyl choride, or dinitrogen tetraoxide.[59] However, it is well known that reagents such as nitrosyl chloride and dinitrogen tetraoxide readily attack double bonds as well as nitrogen.[59] For example, treatment of norbornene (74) with nitrosyl chloride gave the adduct (75).[60] Reaction of (74) with dinitrogen tetraoxide gave the three products (76), (77), and (78).[61]

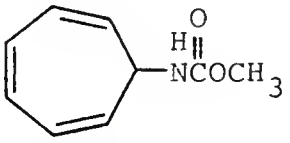


(74) (75)

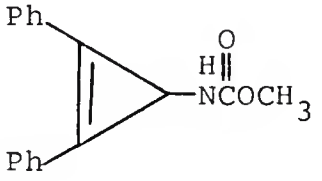


(74) (76) (77) (78)

Nevertheless, Jones and coworkers found that (79) and (80) could be successfully nitrosated with dinitrogen tetraoxide under the correct conditions without disturbing the double bonds.[50,62]

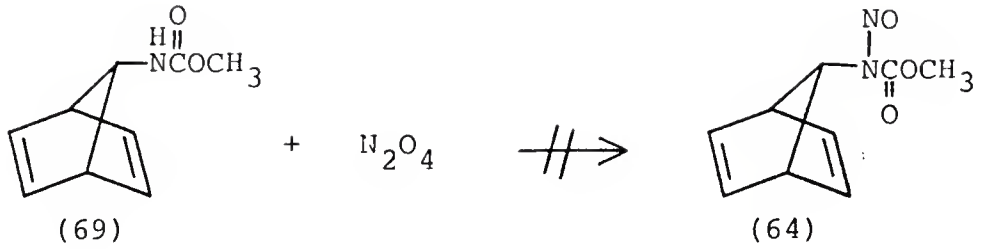


(79)

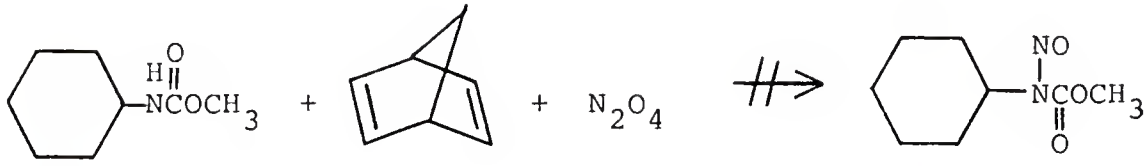


(80)

Therefore, the initial attempts to nitrosate were made using dinitrogen tetraoxide. These experiments were made using either the carbamate (69) or, in order to conserve starting material, a model system consisting of methyl N-cyclohexylcarbamate (81) and (66). A wide variety of conditions were tried in which solvent, temperature, mode of addition of reagents, method of stirring, and other conditions were changed. In all cases only dark brown oils were obtained. No evidence of nitrosation of the nitrogen was found in either (69) or the model system. Clearly, a

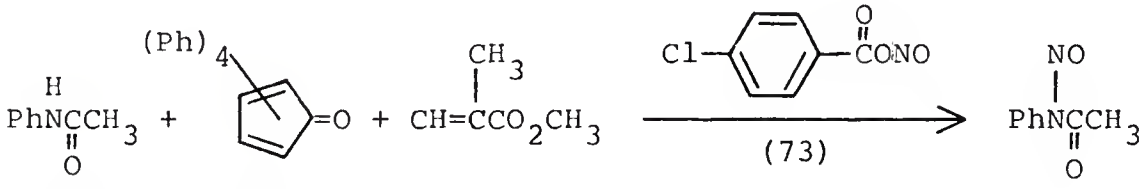


(69) (64)



(81) (66) (82)

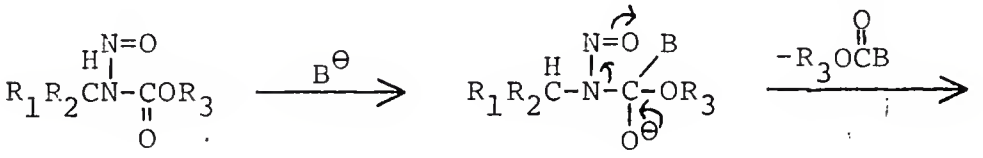
different approach was called for and p-chlorobenzoyl nitrite (73) was chosen as an alternative nitrosating reagent. It was chosen primarily because of its ease of preparation and the fact that it had been successfully employed to nitrosate (83) in the presence of (84) and (85).[63] Indeed, when (73)



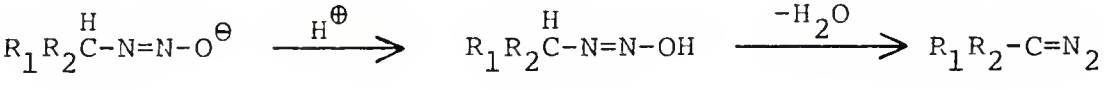
(83) (84) (85) (73) (86)

was used to nitrosate (69) and (70) the successful results reported were obtained. Any explanation offered here for the effectiveness of (73) as a nitrosating reagent would be rather presumptuous.

Generation of diazoalkanes from N-nitroso amide derivatives under basic conditions is a well known process.[47] Also in a few instances diazoalkanes can be generated from them by thermolysis.[51-54] W. M. Jones and coworkers studied the mechanisms involved in both the base and thermal reactions of N-nitroso amide derivatives in detail.[48,52,64] For the base induced decomposition of N-nitroso carbamates Jones found that there are two mechanisms which might come into play depending upon the conditions under which the decomposition is done.[48] However, the important thing concerning diazoalkane production is not which of these mechanisms is being followed but whether a most serious side reaction may occur. Briefly, the two mechanisms which are thought to be involved are as follows. First, the reaction may proceed by initial attack of the base on the carbonyl carbon leading to the diazohydroxide (90) which may then lose water to give the diazoalkane (91). The mechanism by which



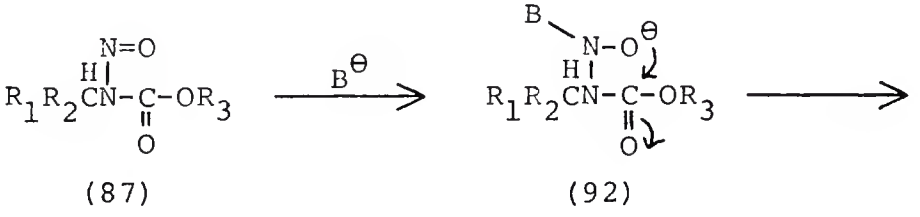
(87) (88)



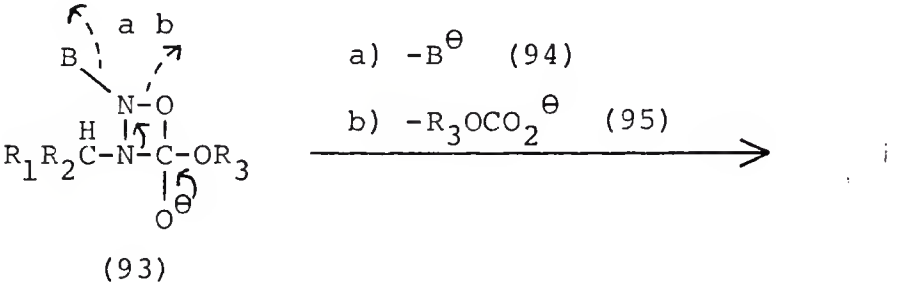
(89) (90) (91)

water is lost is uncertain; however, in any case the hydrogen on the carbon attached to the diazo group must be lost if a

diazoalkane is to be produced. Second, the initial attack of the base may be on the nitroso nitrogen. Loss of either (94) or (95) leads to either (96) or (97) respectively. The intermediates (96) or (97) then may lose either (98) or (99) respectively to give the diazoalkane (91). Which one of these mechanisms is operable depends on the alkyl group, the group attached to the carbonyl carbon atom, the solvent, and the nature of the base.[48] More importantly, the intermediate diazohydroxide (90) or the related intermediates (96) or (97) may give rise to a serious side reaction.



(87) (92)



(93)

a) $-B^{\ominus}$ (94)

b) $-R_3OCO_2^{\ominus}$ (95)

(96) (97)

$-R_3OCO_2H$ (98)

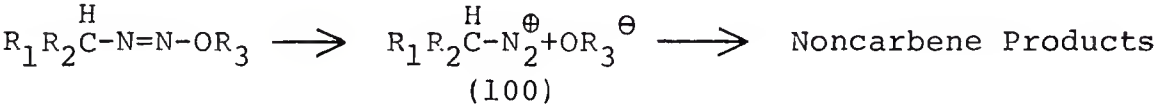
$-BH$ (99)

$R_1R_2C{=}N_2$

(91)

Namely, ionization of (90), (96), or (97) to give the diazonium ion (100) may occur before elimination, by whatever mechanism, of the hydrogen on the carbon attached to the diazo group.[65]

This results in noncarbene products being formed.



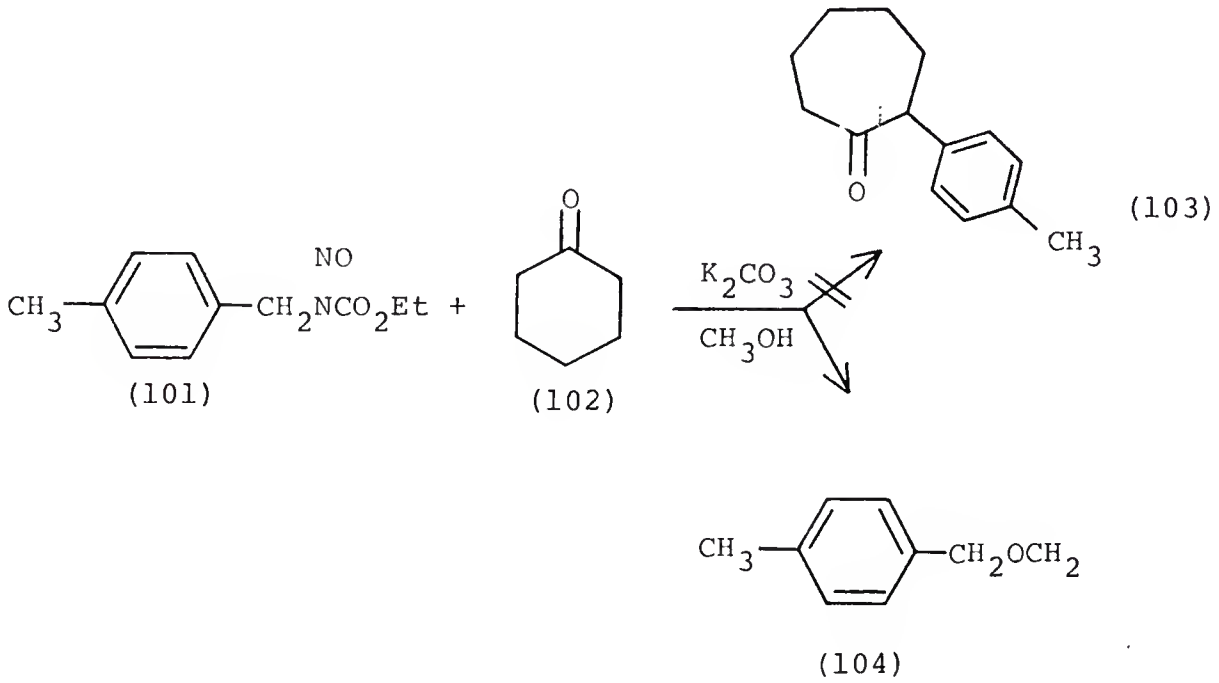
(100)

R_3=H (90)

R_3=CO_2R (96)

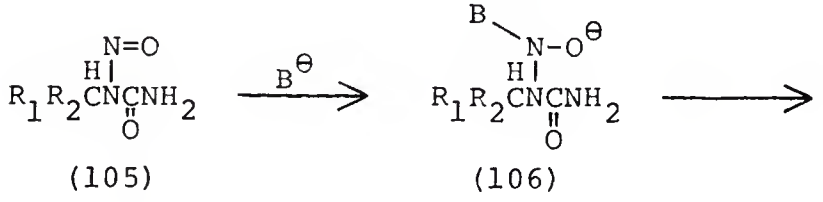
OR_3=B (97)

Unfortunately this is sometimes the case. For example, Gutsche and Johnson found that when (101) was treated with potassium carbonate in methanol in the presence of cyclohexanone (102) the expected product (103) was not isolated. Instead (104) was isolated as the product.[66]

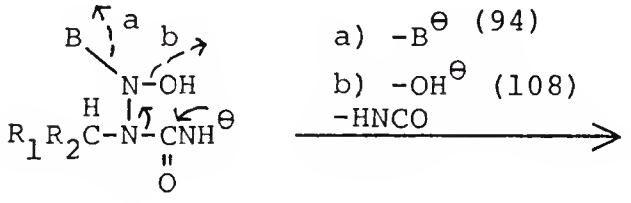


(101) (102) (103) (104)

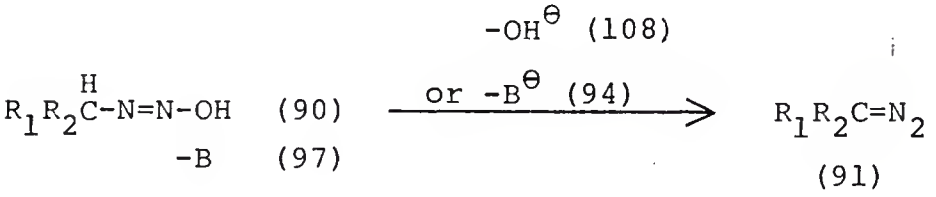
As regards diazoalkane generation from N-nitroso ureas the same side reaction, ionization, may occur whether the decomposition is induced with a base or thermally. For N-nitroso ureas the initial site of attack by the base is thought to be on the nitroso nitrogen to give (106). A proton transfer gives (107) which can lose isocyanic acid to give either (90) or (97) depending on whether route a or b is taken. If (90) or (97) loses (108) or (94) respectively the diazoalkane (91) is the product.[48,64]



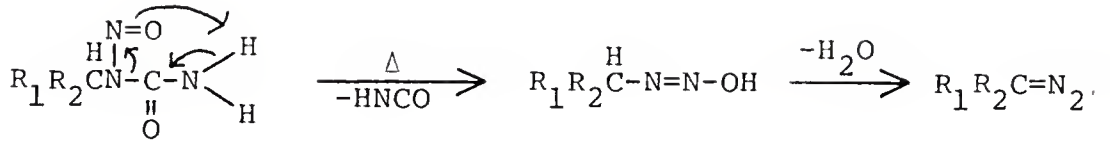
(105) (106)



(107)

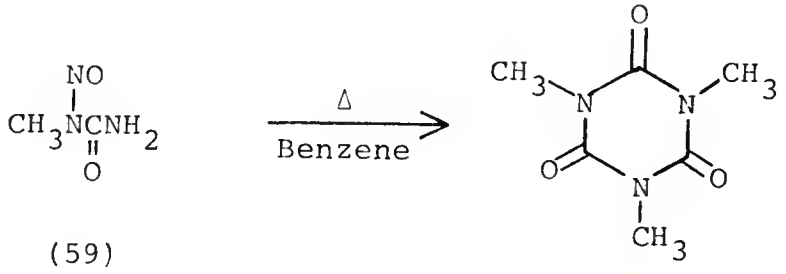


In the case of thermal decomposition of N-nitroso ureas the reaction is thought to involve loss of isocyanic acid to give the diazohydroxide (90).[52] For simplicity this reaction is shown as being concerted. The diazohydroxide may then proceed as discussed previously. At any rate



(105) (90) (91)

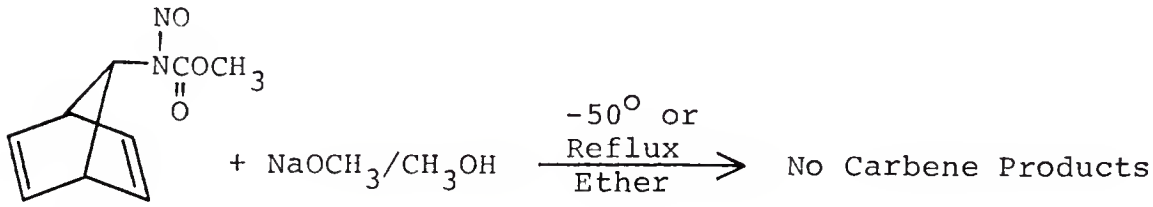
whether base or thermally induced, ionization may take place before the hydrogen on the carbon attached to the diazo group is lost. In addition to ionization there is another problem associated with the thermal reaction. Namely, the isocyanic acid or its trimer (62) produced as a by-product may trap the diazoalkane once it is produced.[52] A reaction of this type was found when Huisgen and Reimlinger decomposed (59) in benzene and isolated (63) as the product.[53]



(59) (63)

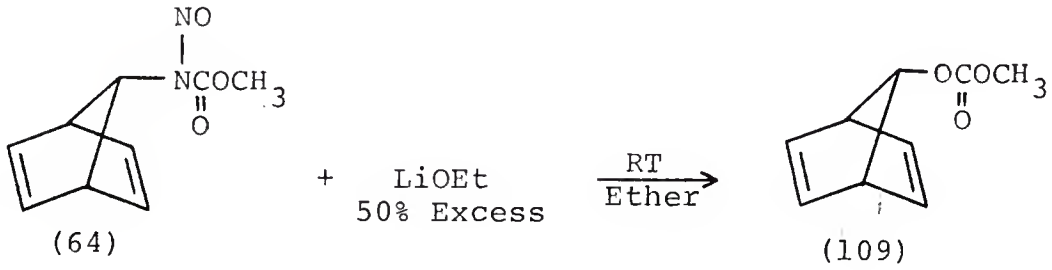
Unfortunately, these problems and possibly others plagued all attempts to generate (1) from (64) or (65) in solution. When (64) was allowed to react with a mixture of sodium methoxide and methanol using ether as a solvent at either -50° or at reflux, only complex mixtures of unidentifiable products were produced. One run was made in the presence of dimethylfumarate in an attempt to trap (1)

if it were present; however, nothing except the product of Michael addition of sodium methoxide to dimethylfumarate was found. In no run was there any evidence found for a carbene product. When (64) was treated with a 50% excess



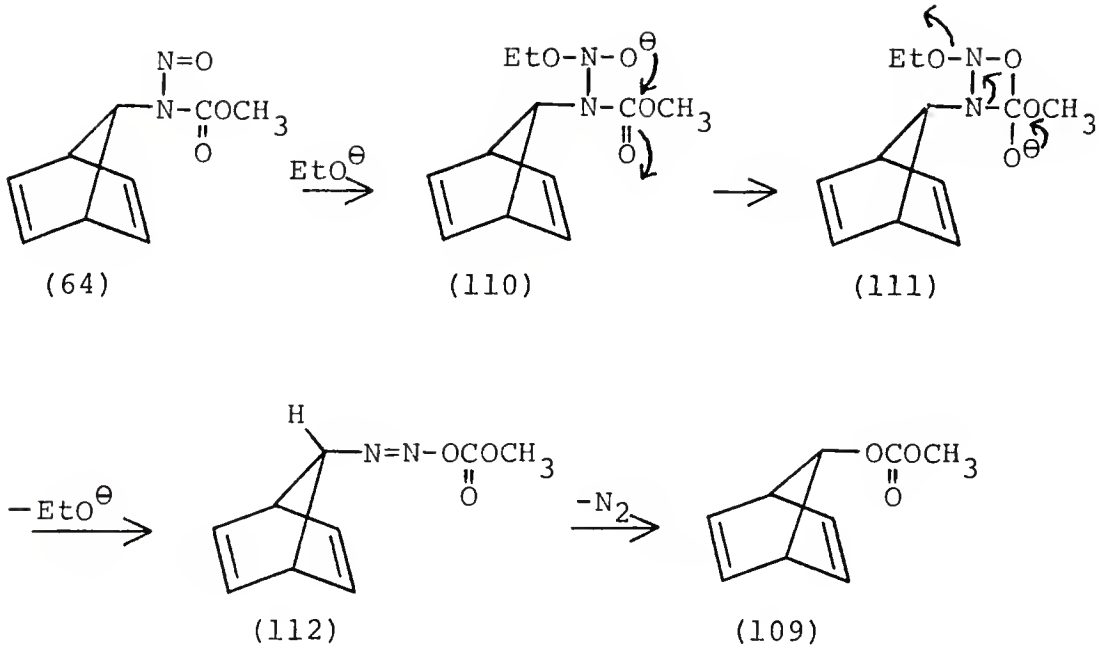
(64)

of lithium ethoxide at room temperature in ether, methyl 7-norbornadienylcarbonate (109) was isolated as the sole product in a 26% yield. This was quite discouraging since

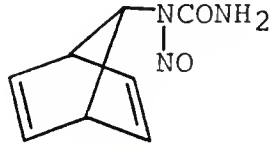


(64) (109)

a product such as (109) is evidence of the ionization side reaction discussed previously. A mechanism which may explain (109) is shown below. When (65) was treated with a variety of bases under a variety of conditions and in some runs in the presence of carbene traps (see Table 1), again only complex mixtures of unidentifiable products were



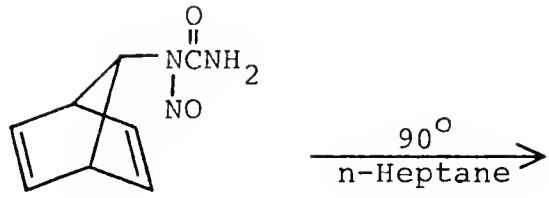
obtained. In no run was there any evidence for a carbene product. At this point attempts to generate (1) via reaction of (64) or (65) with base were abandoned.



(65)

+ Base ⟶ No Carbene Products

Pyrolysis of (65) in n-heptane at 90° under an argon atmosphere gave a mixture of products with the nmr spectrum shown in Figure 1. The presence of 7-norbornadienylisocyanate (68) as one of the products in this mixture is suggested by the multiplets which appear at τ3.1-3.3 and 6.2-6.5 since



(65)

they correlate with the spectrum of authentic (68). As outlined earlier the origin of an isocyanate such as (68) could possibly arise from entrapment of the diazoalkane or conceivably even the carbene by isocyanic acid.[52] Unfortunately, when a reaction was carried out under the same conditions in the presence of excess lithium carbonate no differences in the products were observed. Possibly more interesting than the possible presence of (68) are the other nmr signals in Figure 1. It is believed that these signals τ3.4-3.9 and 6.9-7.1 with an integral ratio of 5 to 2 respectively probably belong to a single material. (In another run under similar conditions an almost identical nmr spectrum (see Figure 2) was obtained of the crude products. However, the integral ratio of the signals at τ3.4-3.9 and 6.9-7.1 was still 5 to 2 whereas the ratio between these signals and the signals at τ3.1-3.3 and 6.2-6.5 was different.)

Presumably, a rearrangement has taken place since the resonance pattern from τ3.4-3.9 no longer resembles the

the pattern so characteristic of the olefinic protons of a norbornadienyl moiety. Quite unfortunately all attempts to isolate this material failed miserably. Even low temperature column chromatography failed. Nevertheless, some insight may be gained into the nature of this material by examining the results of a series of trapping experiments that were run.

In one experiment methanol was added to the crude product mixture and the progress followed by nmr spectroscopy. The nmr spectrum that was obtained is shown in Figure 3. Several observations can be made. The rearranged material reacted rapidly with the methanol. In fact it appears to have reacted faster with the methanol than the material which is presumably (68). In addition when an attempt to isolate the adduct was made via preparative thin layer chromatography only a small amount of the methyl carbamate (69) was obtained.

In another experiment the reaction was carried out in the presence of an excess of dimethylfumarate. The nmr spectrum of the product mixture is shown in Figure 4. The major observation which may be made here is that the fumarate has formed an adduct with something. An attractive explanation would be that it has trapped some material intermediate to the rearranged material. Isolation of this material was foiled by its inadvertent exposure to ethanol. The results of this exposure are shown in Figures 5 and 6. Apparently the new adduct has reacted with the ethanol. An attempt to

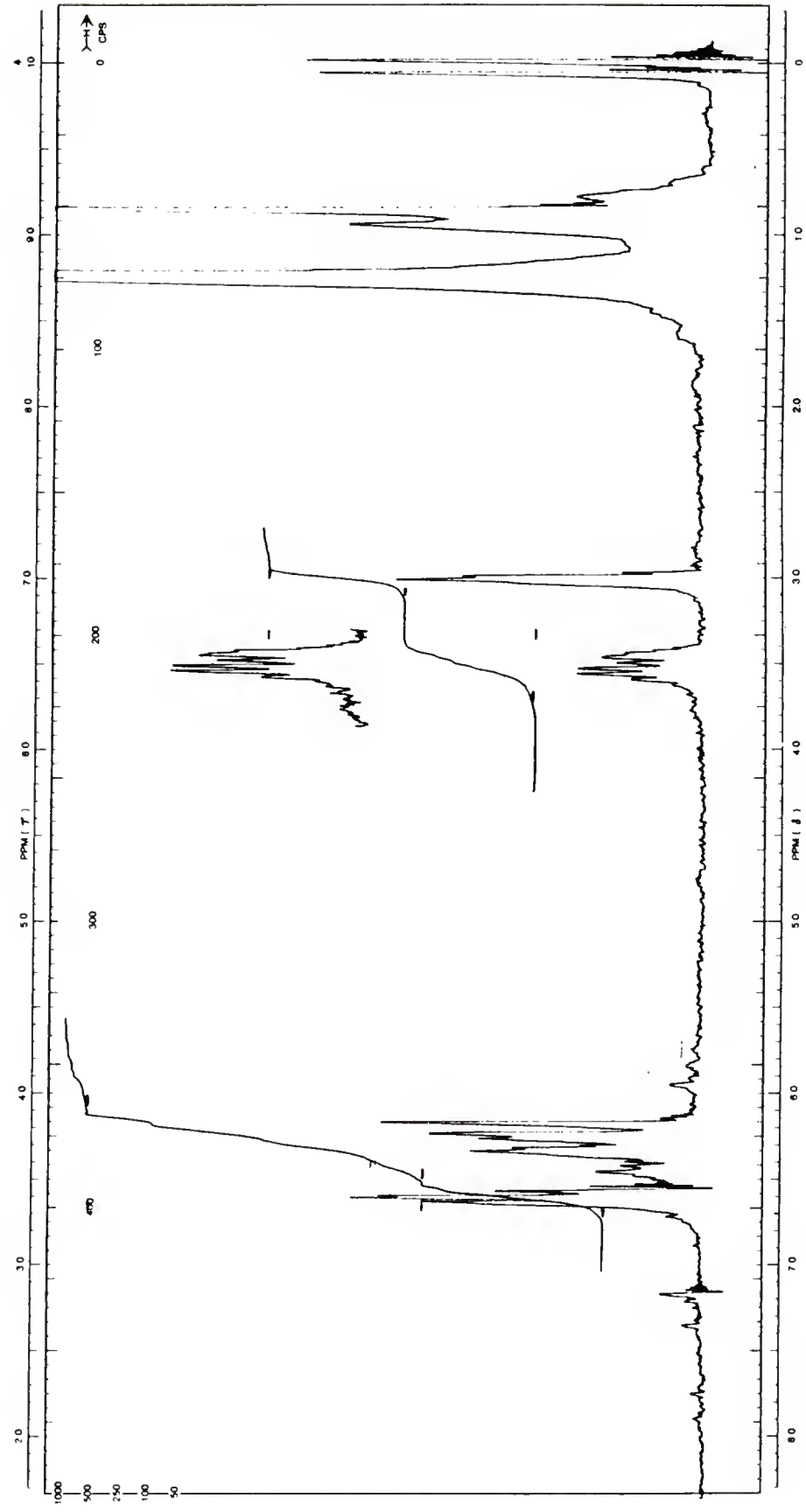


Figure 1

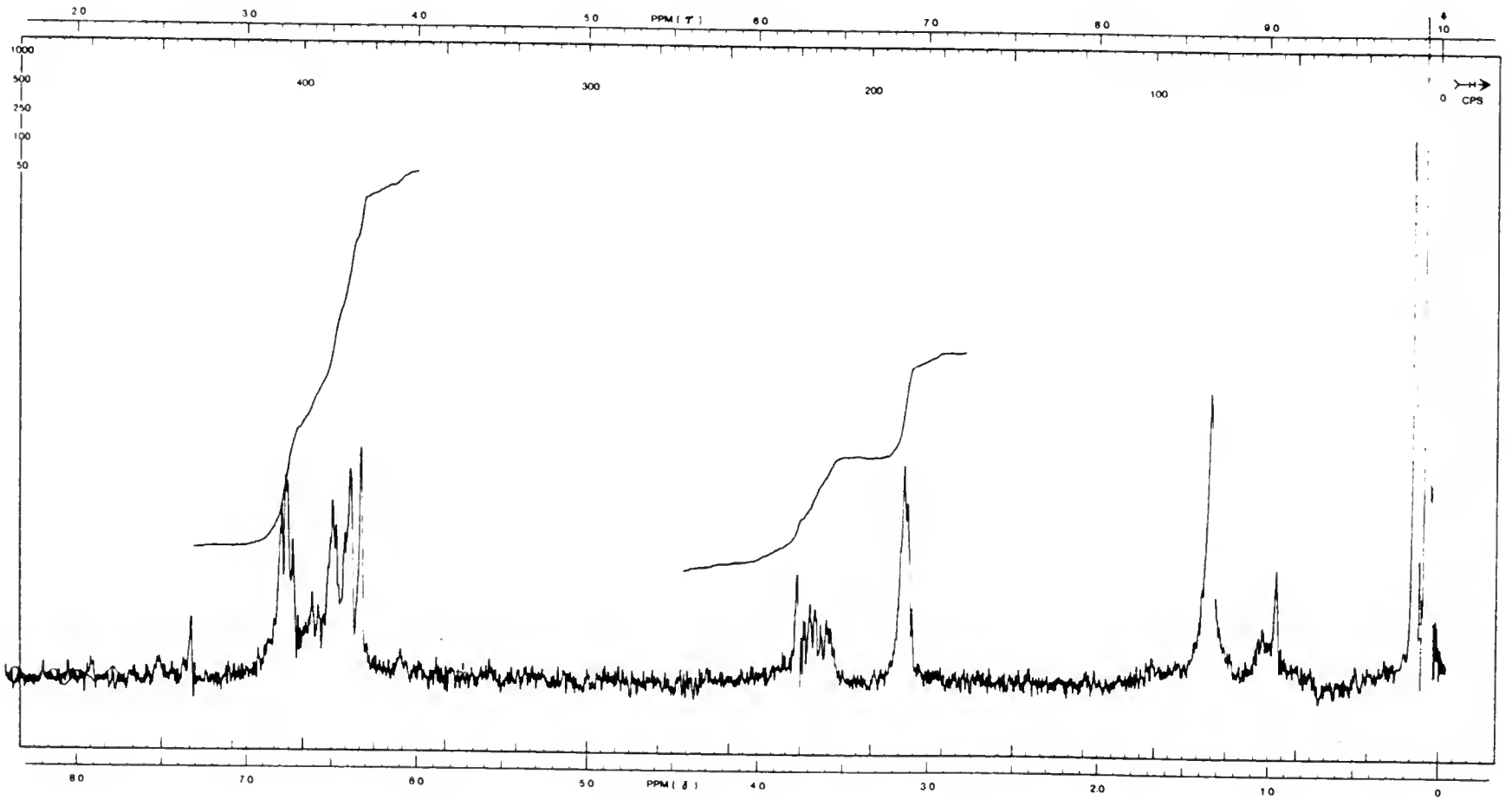
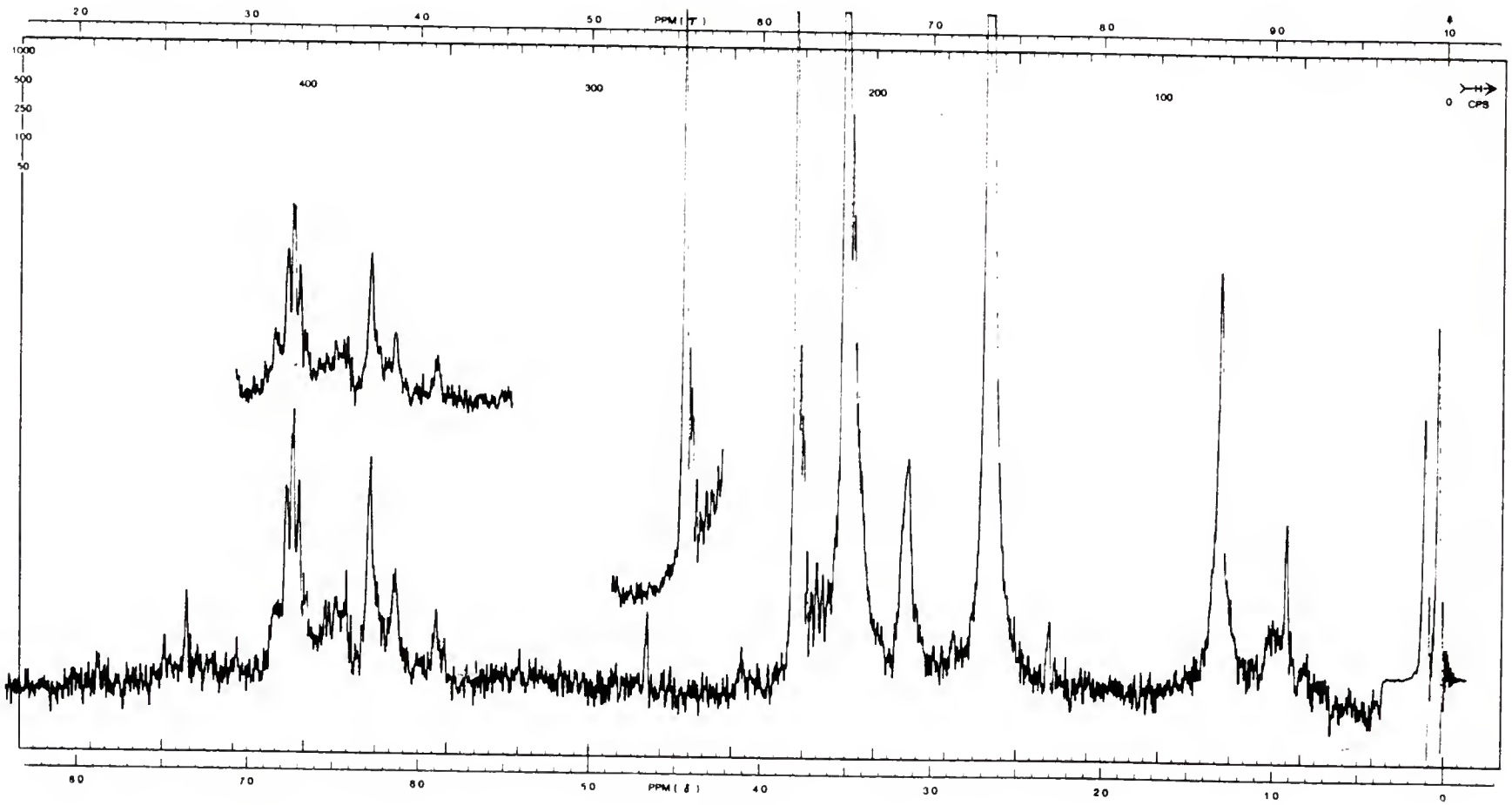

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0
CPS
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Figure 2


20
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40
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PPM (δ)
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80
90
10
1000
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100
50
400
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100
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CPS
80
70
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PPM (δ)
40
30
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10
0

Figure 3

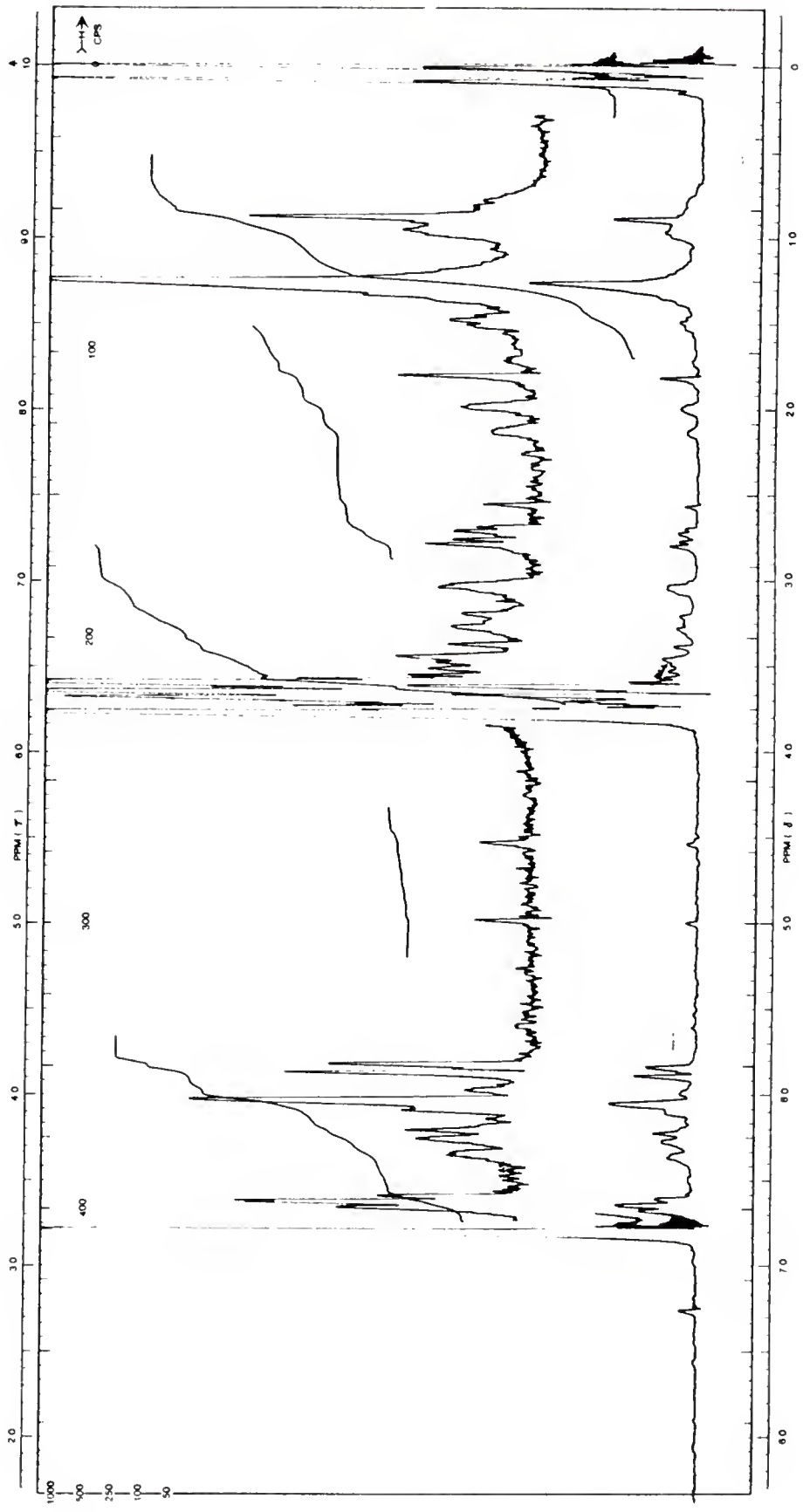
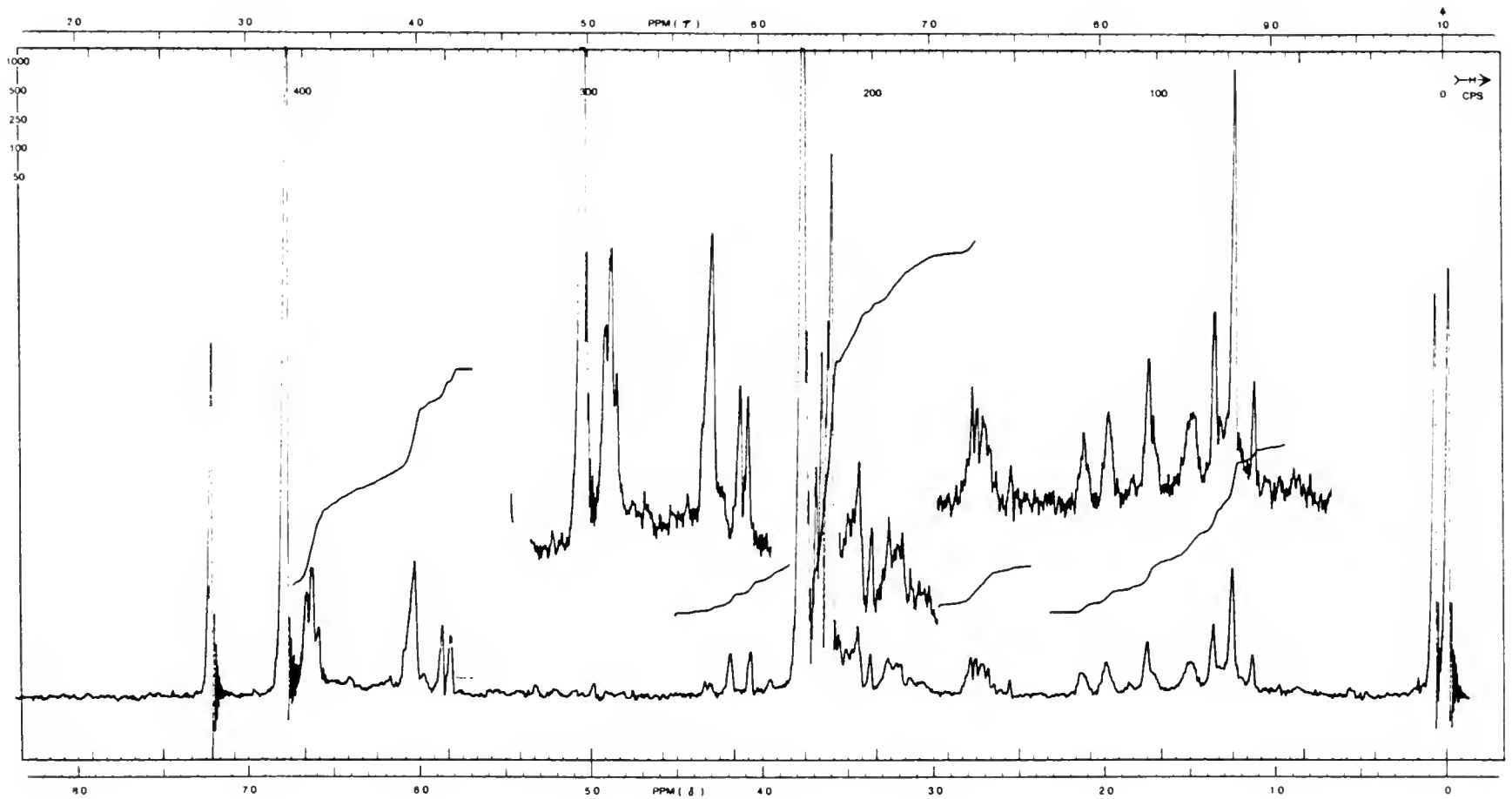


Figure 4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PPM (τ)
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CPS
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PPM (δ)
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10
0

Figure 5

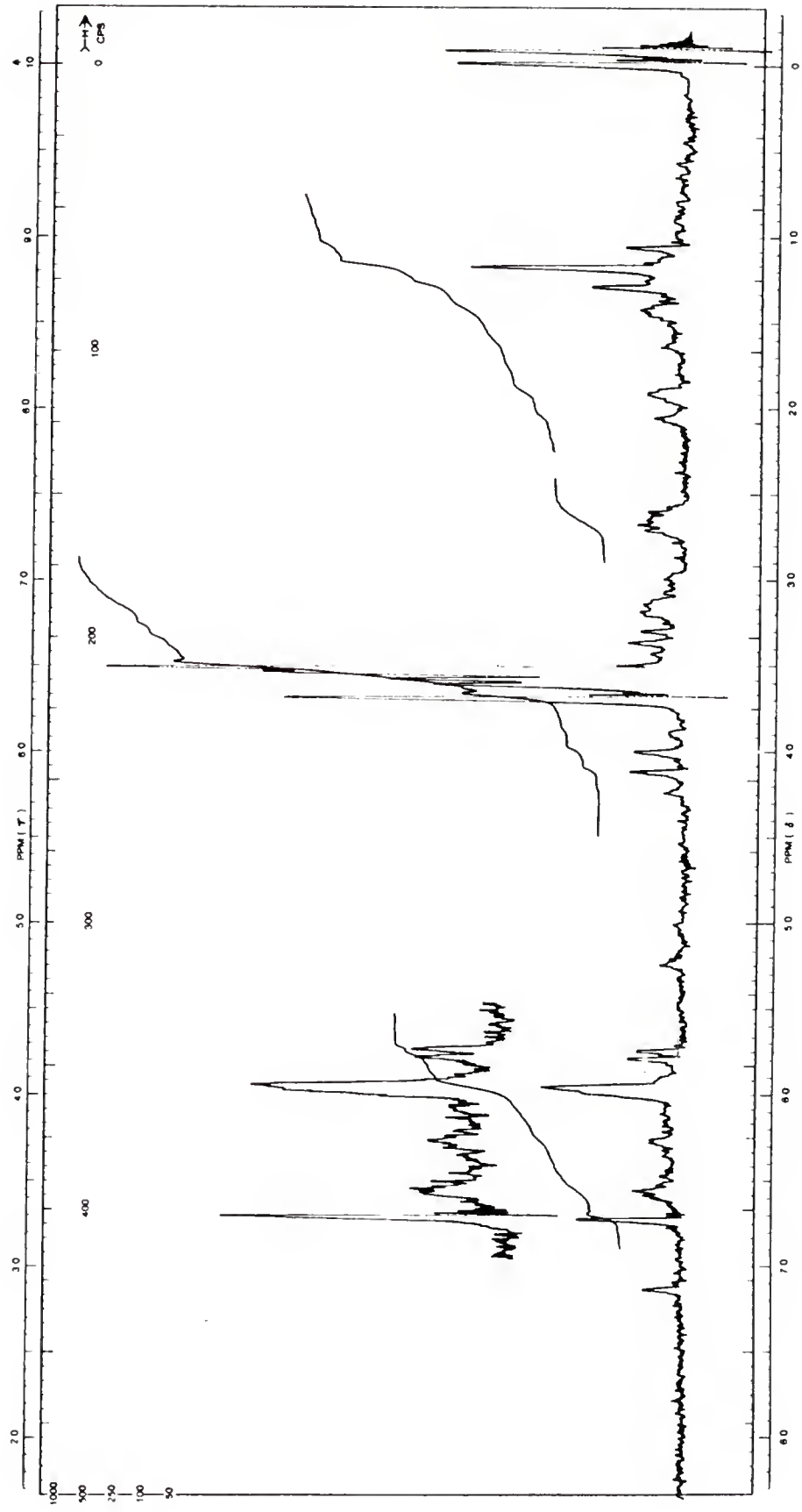
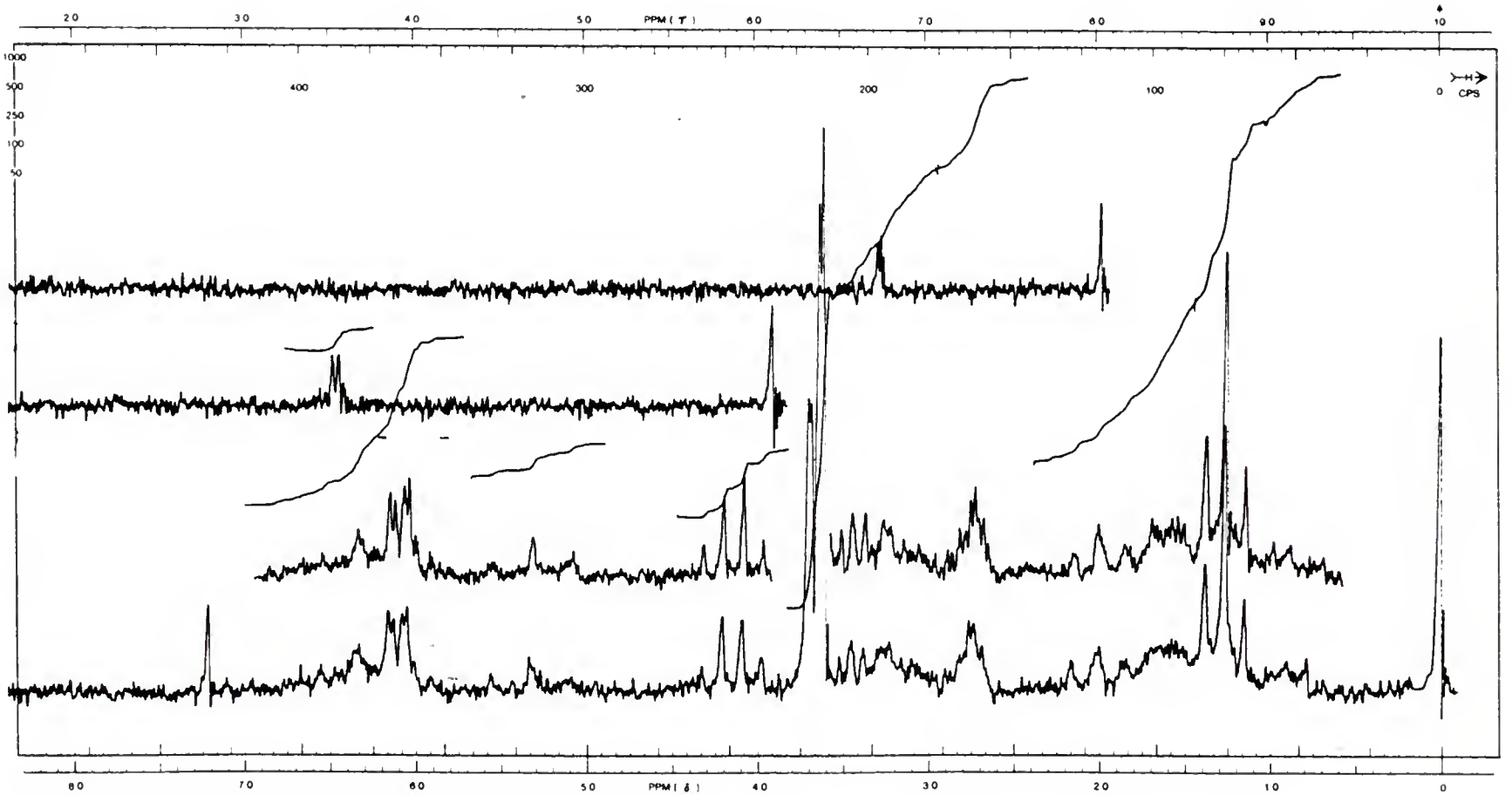


Figure 6


20
30
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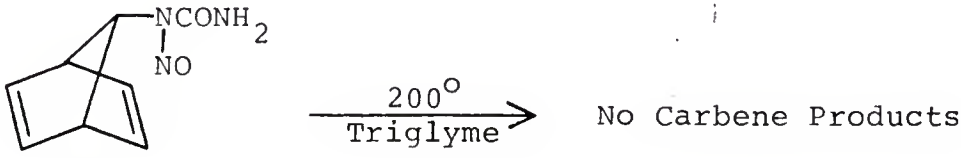
PPM (τ)
60
70
80
90
10
1000
500
250
100
50
400
300
200
100
0
CPS
80
70
60
50
PPM (δ)
40
30
20
10
0

Figure 7

isolate some meaningful material from this mixture *via* column chromatography failed as shown in Figure 7. At this point attempts to identify the rearranged material were stopped mainly for pragmatic reasons and since it was most likely that it was not a carbene product especially in light of the integral ratio of 5 to 2.

A final attempt to generate (1) in solution was made when (65) was thermolyzed in triglyme at 200°. No evidence was obtained for any carbene product. In fact, the only product isolated was a trivial one identified as a contaminant in the triglyme. Therefore, in conclusion, no evidence was found for any carbene type products in any of the experiments that were undertaken in solution although it may be interesting if only for curiosity's sake, to learn the identity of the rearranged material in the heptane experiments.



(65)

With the absence of any evidence for carbene products in any of the solution experiments, gas phase pyrolysis experiments of the N-nitroso urea (65) were initiated. Although a static pyrolysis system would normally have been

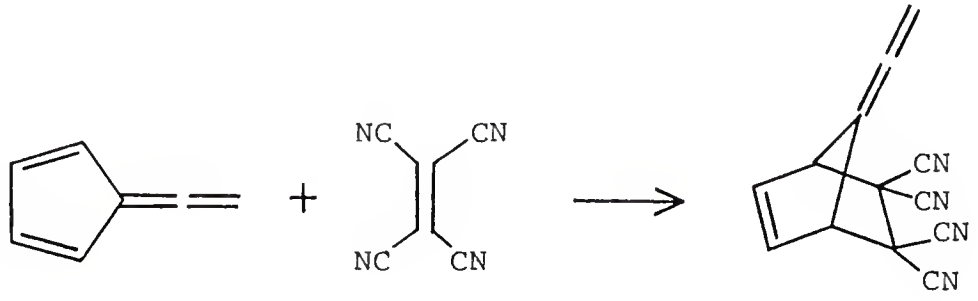
preferred it was not attempted because of the anticipated thermal instability of the expected products. When an attempt was made to thermolyze (65) using the normal method of flash vacuum pyrolysis (the substrate is allowed to slowly sublime through a heated, evacuated tube), no useful results were obtained. Apparently (65) was not volatile enough to sublime, at least without heating relatively strongly, through the pyrolysis tube. With the normal technique of flash vacuum pyrolysis not readily workable another type of flow system was chosen. A system used with success in the past has been the hot tube technique. This technique was used by W. M. Jones and coworkers when they pyrolyzed the sodium salt of benzaldehyde tosylhydrazone (113) to give phenylcarbene (2).[4]

Briefly, the technique consists of dropping the substrate of interest down an inclined tube which is being continuously evacuated and is heated to the desired temperature. In addition the apparatus is continuously swept with a stream of inert gas to help remove products from the hot zone. The products are then condensed in a liquid nitrogen trap. For a detailed description of the procedure used in this work see the Experimental Section.

When (65) was pyrolyzed by the hot tube method at 120° only a complex mixture of unidentifiable products was obtained. No evidence for the presence of any carbene products was found. No further attempts at this temperature were made. However, when (65) was pyrolyzed at higher

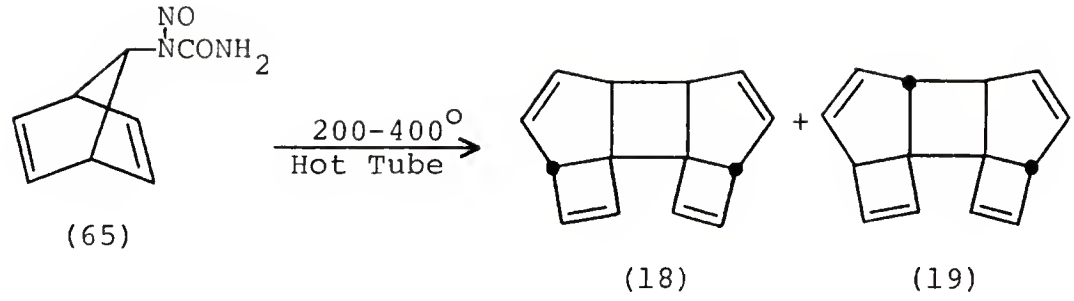
temperatures the results shown in Table 2 were obtained. At 200° a mixture of the isomeric dimers (18) and (19) was obtained in yields of 13% and up. In addition benzene (22) was also formed in yields as high as 19%. Although no quantitative yield was obtained for toluene (23) it was also present in a significant amount (see Note b, Table 2). When the temperature was raised to 250° (18) and (19) were again isolated in yields exceeding 14%. In addition heptafulvalene (14) was found in one run in a 5% yield. Again benzene and toluene were products in yields of 18 and 4% respectively. At 300° a trend began to appear. The dimers (18) and (19) were found in yields from 9 to 14% whereas heptafulvalene (14) was found in yields from 6 to 15%. The yield of benzene was typically 3 to 4% but toluene was not observed in any of the experiments at this temperature. At 350° the trend continued. The dimers (18) and (19) were no longer present in the product mixture. The yield of heptafulvalene (14) had increased to above 18%. Again benzene was a product but no toluene. No evidence was found for either heptafulvalene (14) or the dimers (18) and (19). That (14) was not simply decomposing at 400° was shown when authentic (14) was pyrolyzed at 400° and recovered in a 32% yield. In a typical experiment at 400° the only products identified were benzene in yields of 3% and better and some aromatic hydrocarbons in an undetermined amount. A few of these hydrocarbons have been identified by gc-ms as biphenyl, bibenzyl, and two materials with molecular formulae of $C_{14}H_{12}$. That similar aromatic hydrocarbons were also formed at the lower temperatures was suggested by nmr

resonances in their analyses that were similar to resonances found in 400° nmr analyses. In addition, in one experiment not shown in Table 2 the volatile constituent of the product mixture was allowed to react with tetracyanoethylene (TCNE), a known fulveneallene (12) trap.[6] When the products from this reaction were analyzed by nmr some weak signals corresponding to those reported in the literature[6] for 5,5,6,6-tetracyano-7-vinylidenebicyclo[2.2.1]hept-2-ene (114) were found. However, the yield was too low to be quantified. Nevertheless, the presence of (12) as a product at 400° was strongly suggested. To summarize quickly, the isomeric

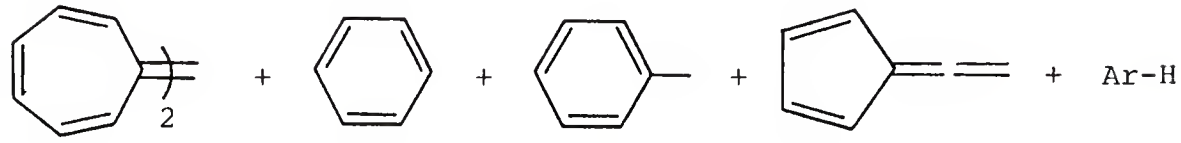


(12) (114)

dimers (18) and (19) were obtained from 200 to 300°; hepta-fulvalene (14) from 250 to 350°; benzene from 200° and up; toluene at 200 and 250°; and at 400° benzene, a mixture of aromatic hydrocarbons, and most likely fulveneallene (12). In addition similar aromatic hydrocarbons may have been present at the lower temperatures.

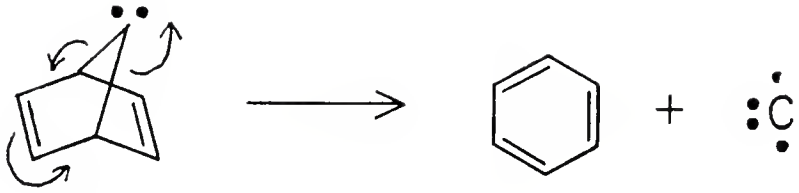


(65) (18) (19)



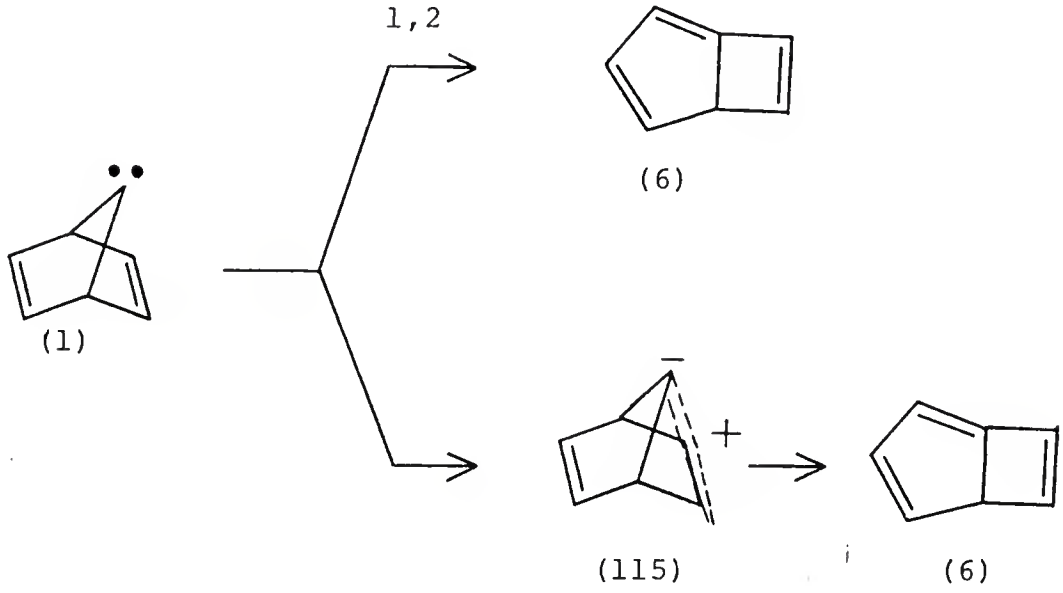
(14) (22) (23) (12)

These results suggest an attractive mechanism. Pyrolysis of the N-nitroso urea (65) above 200° may lead to 7-norbornadienylidene (1). This carbene may then fragment to give benzene and a carbon atom in a manner similar to that which Wolf and Shevlin found when they generated quadricyclanylidene (7).[8] This is supported by the isolation of (22) and (23). Rearrangement of (1) to (7) is not likely since from simple thermochemical considerations (7) is calculated to be 40 kcal/mole higher energy than (1). Instead of fragmenting (1) may also rearrange to the bicyclic triene (6) by a reaction that is formally a 1,2 carbene shift. This rearrangement of course parallels the reaction which Moss and coworkers found when they generated 7-norbornenylidene (24) to give (25) as a major product.[28] As to whether the mechanism for rearrangement is a 1,2 shift or involves a nonclassical intermediate is, however, open to question.



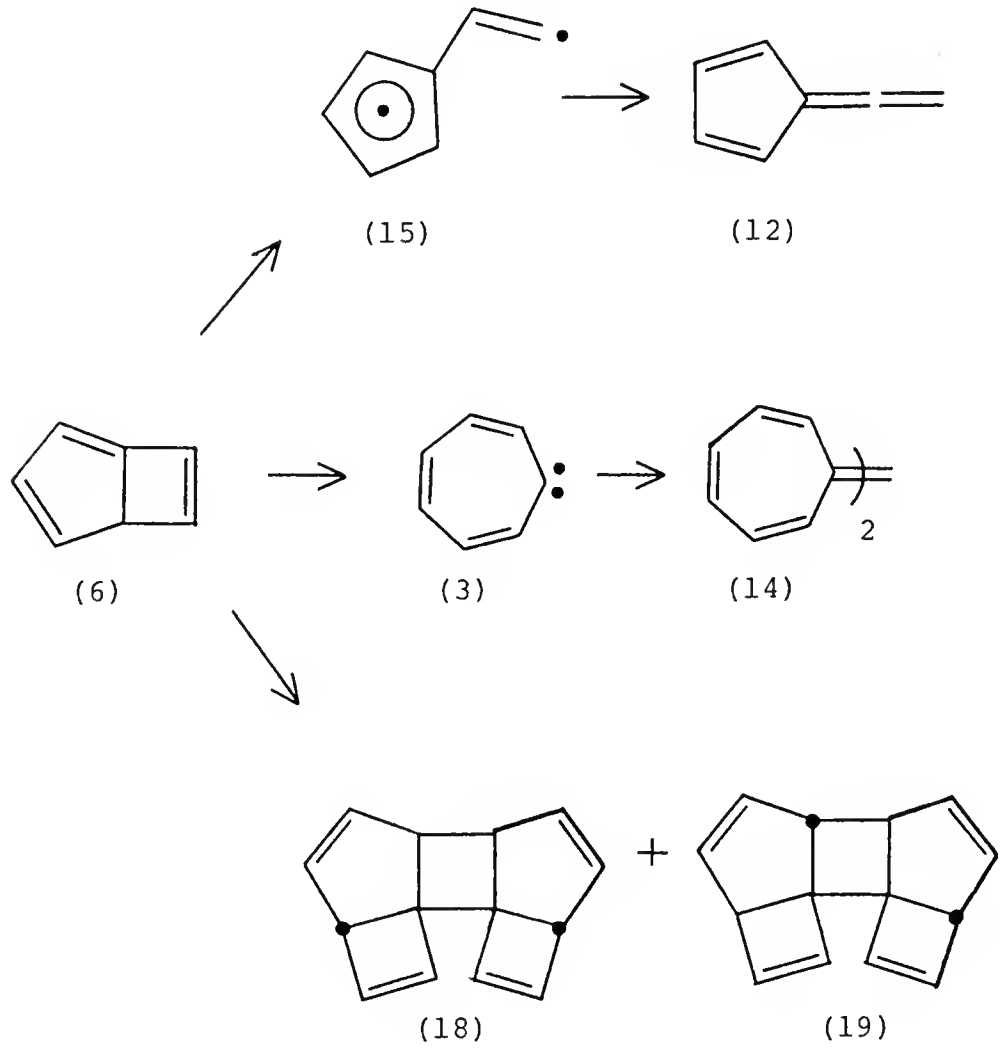
(1) (22)

Apparently the fate of the bicyclic triene (6) is dependent on the temperature. Below 300° dimerization

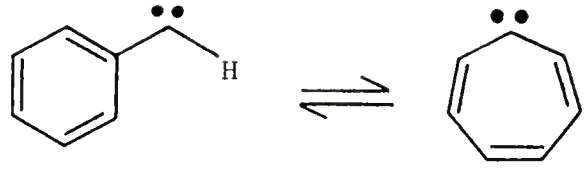


may occur to give the isolated isomers (18) and (19). In addition if the temperature is between 250 and 350° rearrangement of (6) to cycloheptatrienylidene (3) may occur. Dimerization of (3) then accounts for the observed heptafulvalene (14). The trapping experiment with TCNE at 400° suggests that at this temperature (6) may be rearranging to fulveneallene (12). Rearrangement of (6) to (3) and

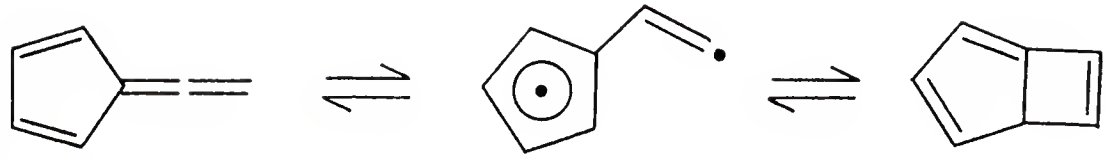
(12) gains support from the recent work of Wentrup and coworkers whose ^{13}C labeling experiments with phenyl-



carbene (2) and fulveneallene (12) are most easily explained by a mechanism involving interconversion of (6), (3), and (12).[21] To summarize, an attractive scheme which would explain all of these results is as follows: the carbene (1) either fragments to give (22) and a carbon atom or rearranges to (6) which depending on the temperature dimerizes, rearranges to (3), or rearranges to (12).

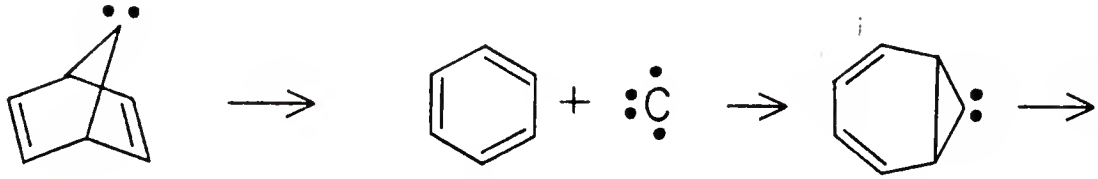


(2) (3)

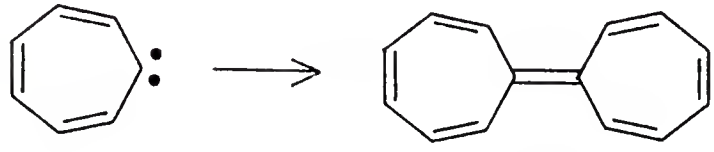


(12) (15) (6)

However, there are a number of alternative mechanisms which come to mind that could at least explain portions of the results. These include the following: One, fragmentation of (1) may give benzene and a carbon atom which could combine to give (27). Rearrangement of (27) to (3) and subsequent dimerization of (3) would explain the

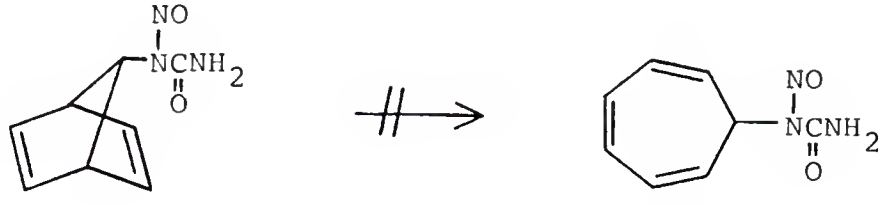


(1) (22) (27)



(3) (14)

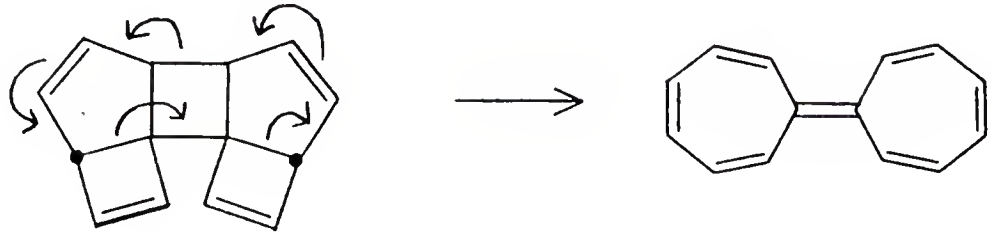
heptafulvalene (14). In fact, there are examples in the literature where carbon atoms generated from an arc or in an accelerator have reacted with benzene to give products which suggested a mechanism involving addition of the carbon atom to (22) to give (27) and subsequent rearrangement to (3).[22] However, the fact that benzene (22) and (14) do not always appear simultaneously as products, as one might expect if this mechanism were important in the chemistry of the N-nitroso urea (65), casts doubt upon the validity of this mechanism in this case. Two, (1) may rearrange to norcaradienylidene (27) by direct rearrangement. This would be a retro-Skattebøl rearrangement.[22] However, as mentioned before there is no literature precedent for a reaction such as this. Three, it is possible that (65) could rearrange to (116) which, in turn, could give heptafulvalene (14). That (65) does not rearrange to (116) is shown by Jones and Manganiello who find that (116) does not give any (14) when pyrolyzed under the same conditions as used in this work.[67] Four, phenylcarbene (2) could account



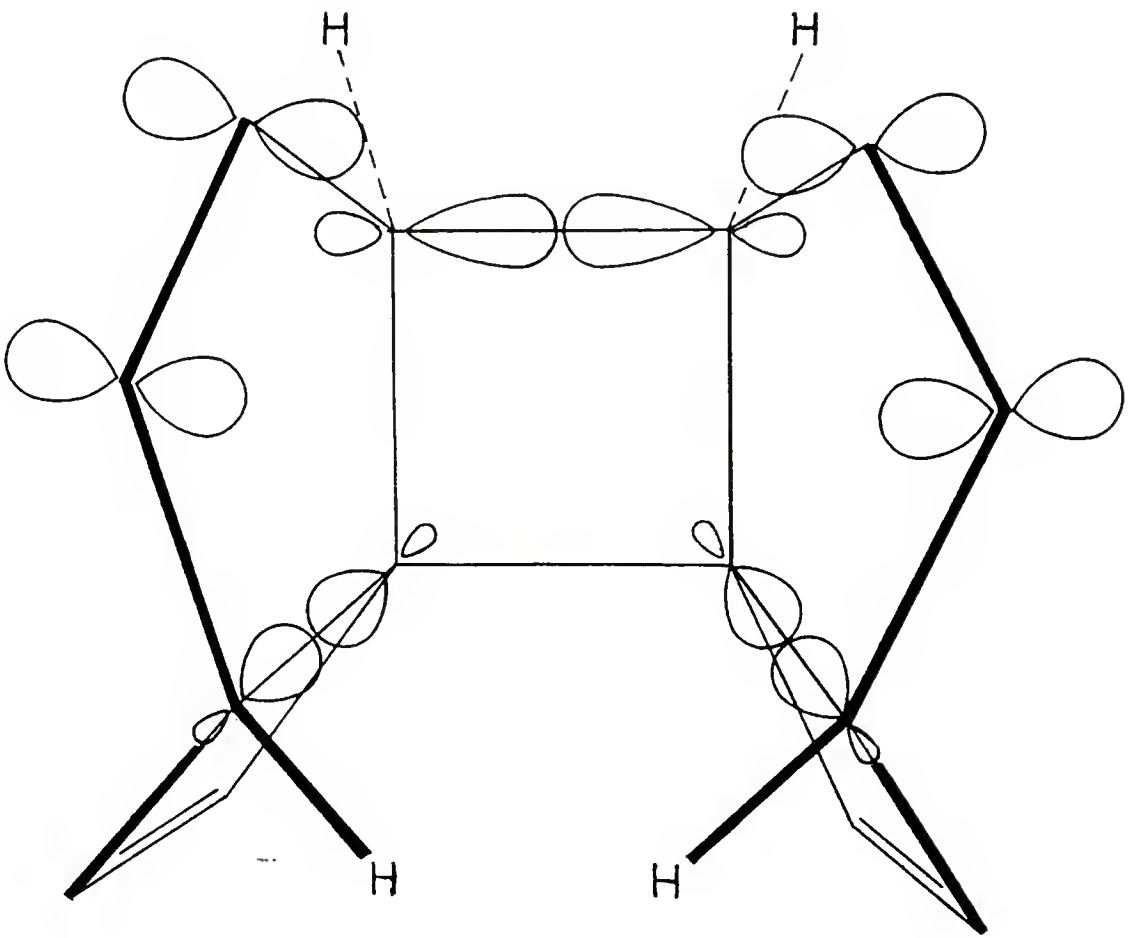
(65) (116)

for the formation of (14) from 250 and 350°. However, the fact that (14) is no longer a product at 400° while authentic (2) generated at 400° gives a 33% yield of (14) casts some doubt on the importance of this possibility although it does not entirely rule it out.

Five, electrocyclic ring opening of (18) to (14) is in principle a plausible alternative mechanism for explaining the increasing yield of (14) with temperature. This rearrangement is particularly interesting because according to the Woodward Hoffman rules the reaction is allowed for the syn isomer (18) and not allowed for the anti isomer (19).[68] In theory then the observation that (18) is being selectively depleted as the temperature is raised would be evidence for this rearrangement. Unfortunately, it was not possible to obtain conclusive evidence for or against depletion of (18) in the experiments undertaken in this work. Nevertheless, it is possible to exclude this mechanism. When an authentic mixture of (18) and (19) was pyrolyzed at the temperature which should have yielded the highest yield of (14), 350°, no (14) could be found by nmr analysis.



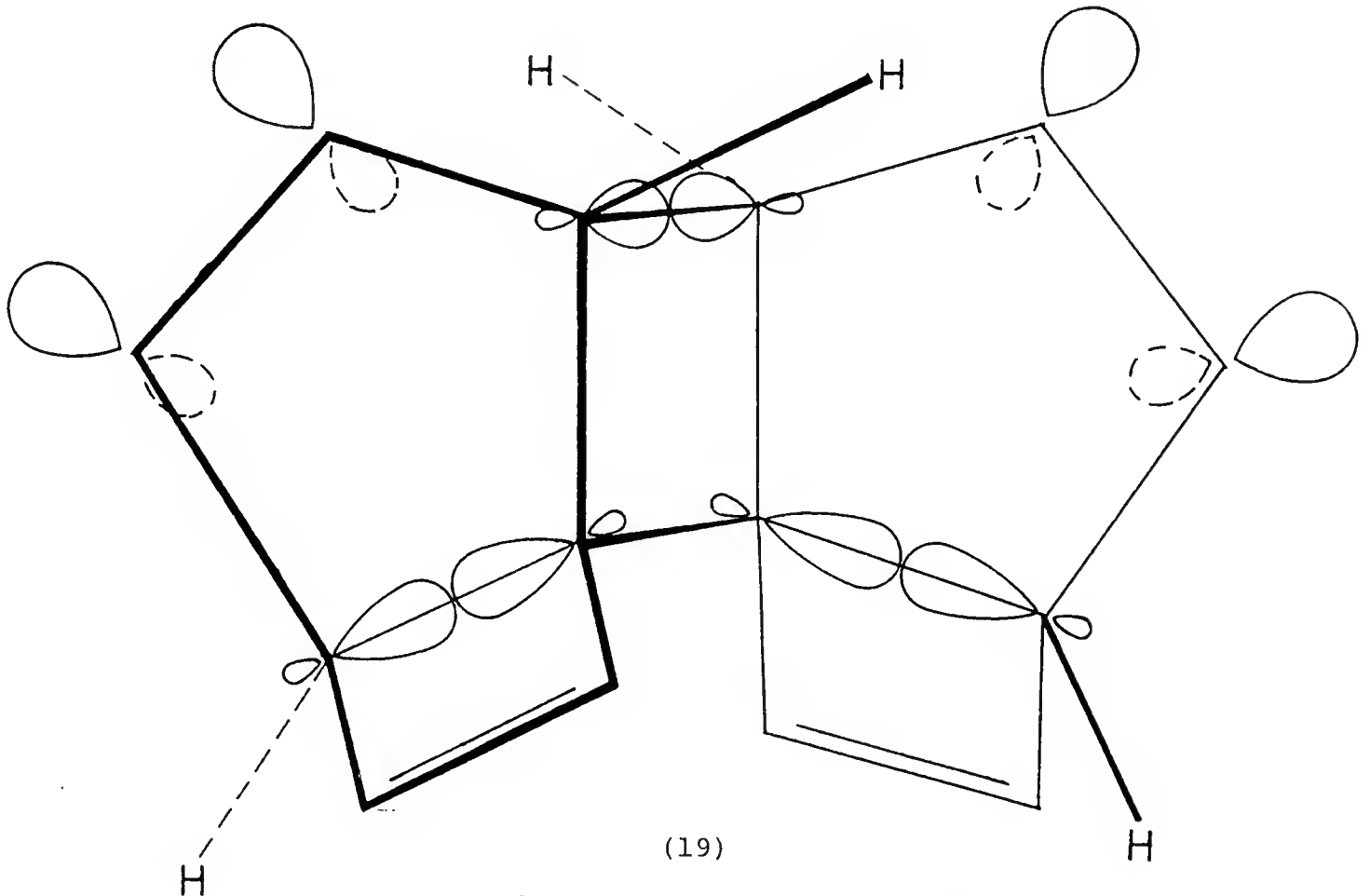
(18) (14)



(18)

$$6^2s + \pi^2s + 6^2s + \pi^2s + 6^2s$$

Symmetry Allowed

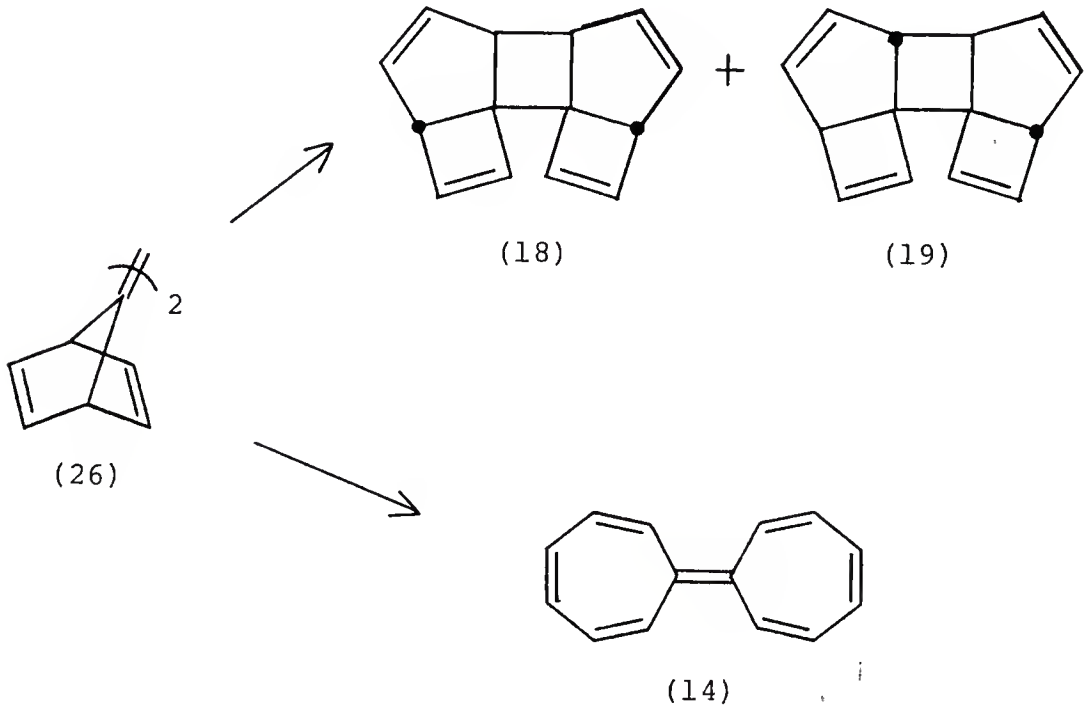


(19)

$6^2a + \pi^2s + 6^2s + \pi^2s + 6^2s$

Symmetry Forbidden

Six, in none of the pyrolysis experiments is there any evidence for binorbornadienylidene (26).[69] On the other hand it is conceivable that dimerization of (1) to (26) may occur followed by rearrangement of (26) to (14) or rearrangement to (18) and (19). Of course rearrangement of (26) to (14) would have to be favored at higher temperatures in order for this mechanism to be consistent with the experimental results obtained. Although norbornadienyl compounds are



(18) (19)

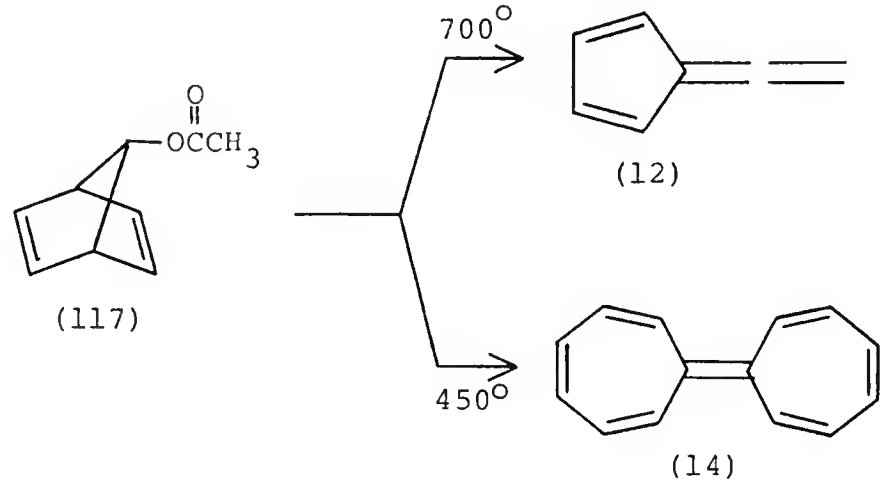
(26)

(14)

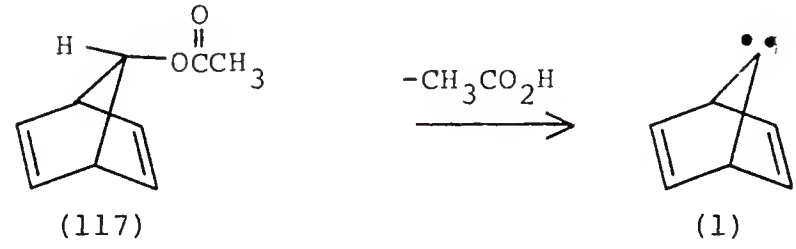
known to rearrange to cycloheptatrienyl compounds[70] on heating, not much is contained in the literature on the thermal stability of methylene norbornadienes. Although in one instance Martin and Forster report that dimethyl methylenenorbornadiene is stable at 100° for 24 hours.[71]

Seven, an interesting possibility although admittedly rather wild, comes to light when the recent results of R.

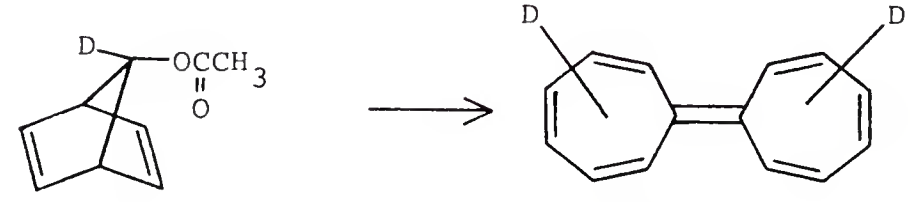
Hoffman[21,72,73] and those of Chan and Massuda[74] are viewed along side the results in this work. R. Hoffman found that when 7-acetoxynorbornadiene (117) was subjected to flash vacuum pyrolysis at 450° and 700° acetic acid and heptafulvalene (14) or fulveneallene (12) respectively were obtained as products.[21] An attractive explanation for this would have been generation of (1) which then could have led to (14) and (12). However, when (117d) was pyrolyzed at 450° (14d) was isolated still containing most of the



(117) (12) (14)

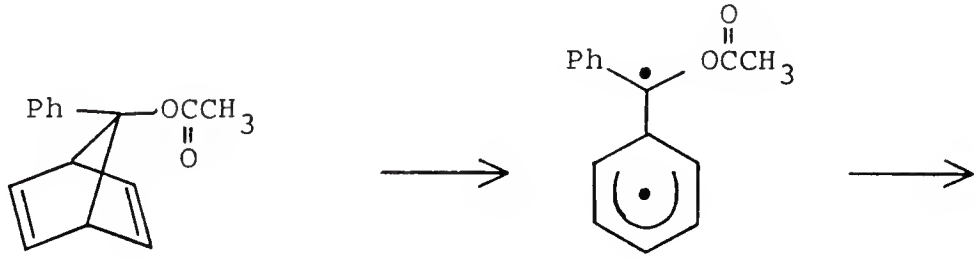


(117) (1)



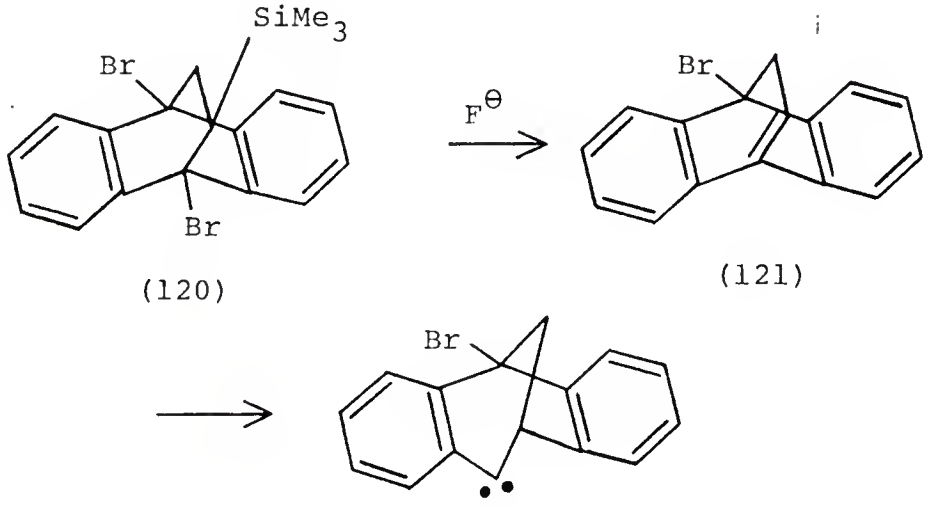
(117d) (14d)

deuterium.[72] Therefore, (1) could not have been involved. Hoffman and coworkers have proposed a free radical mechanism to explain the products obtained in the case of 7-phenyl-7-acetoxynorbornadiene (118).[73] Chan and Massuda found



(118) (119)

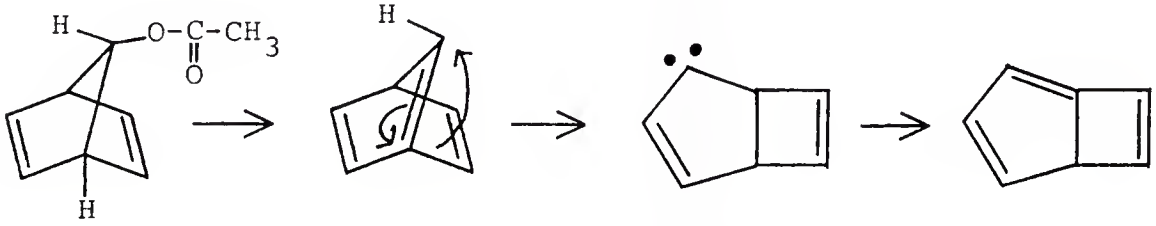
strong evidence when (120) was treated with fluoride ion for the formation of the bridgehead olefin (121) and what is apparently a retro 1,2 carbene shift to give the carbene (122).[74] They were able to trap both of these intermediates with appropriate traps. Therefore, it is conceivable that decomposition of (117) could proceed by elimination across



(120) (121)

(122)

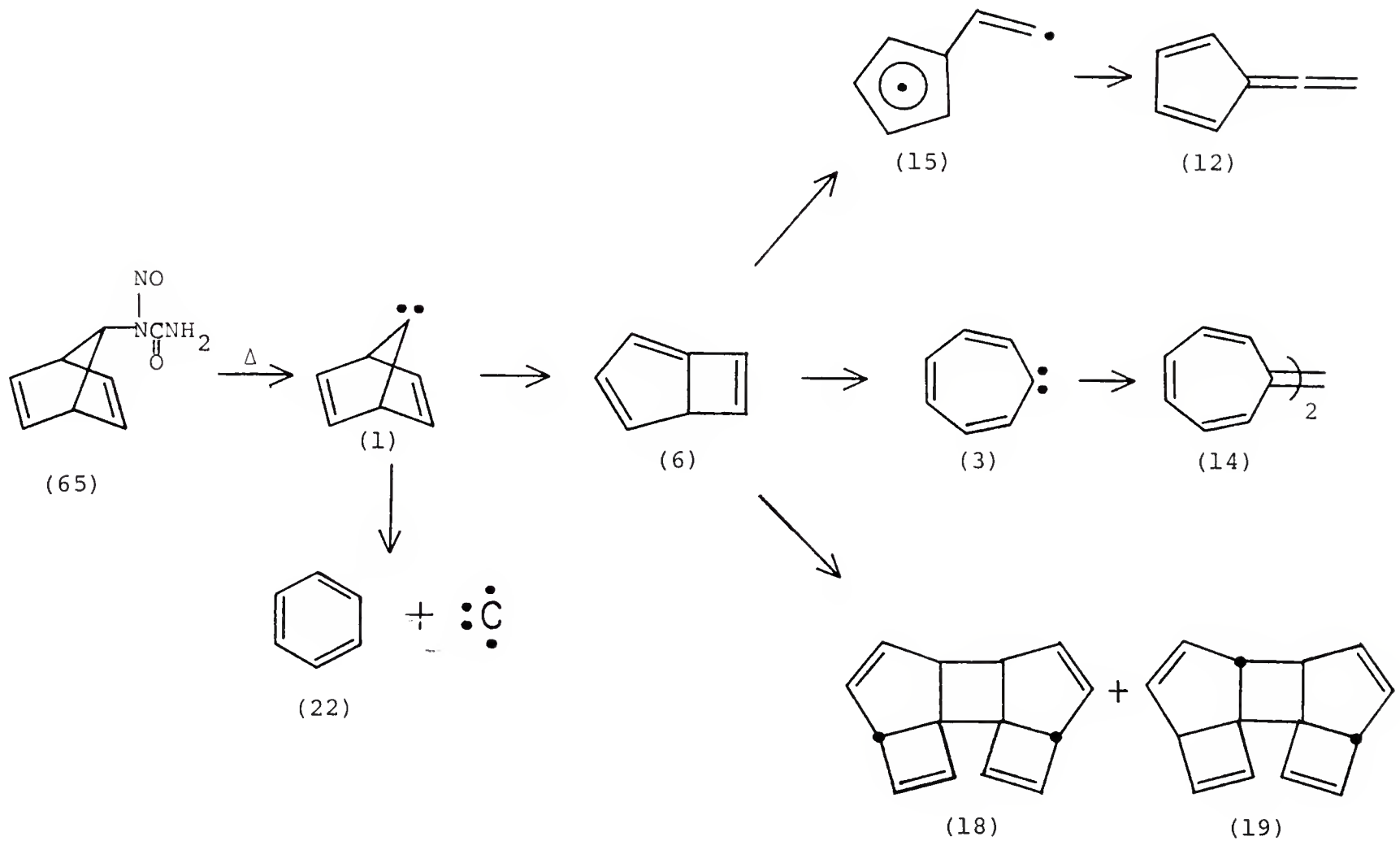
the 1,7 bond of (117) to give the very strained anti-Bredt compound bicyclo[2.2.1]hepta-1,2,5-triene (123). This could then rearrange to 4-bicyclo[3.2.0]hepta-2,6-dienylidene (124) via a retro 1,2 carbene shift followed by a 1,2 shift to give (6). Of course a deuterium on the 7 position would still be contained in the products. In addition it is also possible that some intermediate in the case of (65) could undergo the same process. As to whether this mechanism is of importance remains to be seen. However, it should be noted



(117) (123) (124) (6)

that an interesting dilemma surfaces if (117) is giving rise to (123) assuming that temperatures are directly comparable between the hot tube experiments and Hoffman's experiments. That is, how could (6) give rise to heptafulvalene (14) at 450° in the case of (117) and give no (14) at 400° in the case of the N-nitroso urea (65)?

In conclusion, (1) is strongly suggested as an intermediate in the hot tube pyrolysis experiments. The mechanism that is most consistent with the current literature and experimental evidence is one involving rearrangement of (1) to


NO
NCNH2
O
Δ
(65)
(1)
(6)
(15)
(12)
(3)
(14)
2
(22)
+ :C:
(18)
+
(19)

(6) followed by, depending on the temperature, dimerization to give (18) and (19) or rearrangement to give (3) or (12). Nevertheless, mechanisms involving (2), (26) or (123) cannot be entirely ruled out.

EXPERIMENTAL

General. All melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. All 60 MHz nuclear magnetic resonance data were obtained on a Varian A-60A spectrometer and are reported in units of τ from tetramethylsilane which was used as an internal standard. The 100 MHz nuclear magnetic resonance data were obtained on a Varian XL 100 spectrometer and are reported in the same manner. Infrared data were obtained on either a Beckman IR 10 or Perkin-Elmer 137 spectrophotometer. Ultraviolet spectra were obtained on a Cary 15 spectrophotometer. Combustion analyses were performed by Atlantic Microlab Inc., Atlanta, Georgia. Mass spectra were obtained on an AEI MS 30 spectrometer.

Analytical thin layer chromatographies were performed on either Eastman silica gel or alumina chromatograms impregnated with florescent indicator. Preparative thin layer chromatographies were carried out on 8 in. x 8 in. silica gel plates coated to a thickness of 1.0 mm with Merk PF 254 preparative thin layer chromatography silica gel. Unless otherwise noted solvents were reagent grade and were used as obtained.

7-t-Butoxynorbornadiene (67). This material was either used as obtained from Frinton Laboratories Inc.,

Vineland, New Jersey, or was prepared according to the method of P. R. Story and S. R. Fahrenholtz.[55]

7-Chloronorbornadiene (50). 7-Chloronorbornadiene (50) was prepared by the method of P. R. Story and M. Saunders[56] with the following modifications. The reaction solution was cooled with an ice water bath while the initial hydrogen chloride was bubbled in. In addition, instead of distilling the product on a spinning band column a 30 cm Vigreux column was used to give a product which was essentially pure except for acetic anhydride. The amount of acetic anhydride was reduced to an acceptable level by chromatography with pentane on a silica gel column.

The spectral data were as follows: NMR ($CDCl_3$) τ3.2-3.5 (m, 4H, olefinic), 5.7-5.9 (m, 1H, C-7), 6.3-6.5 (m, 2H, bridgehead); ir (neat) 3130, 3110, 3080, 3000, 1650, 1550, 1370, 1310, 1200, 950, 880, 810, 730, 650 cm^{-1} on Beckman IR 10.

Silver Isocyanate (71). This procedure is essentially that of Birkenbach and Linhard[58] with some refinements. The entire preparation was carried out in the dark and the product was protected from light at all times. To a solution of 34.0 g (0.20 mol) of silver nitrate in 1000 ml of deionized water in an amber bottle was added a solution of 17.9 g (0.22 mol) of potassium cyanate in 1000 ml of deionized water. The potassium cyanate solution had been previously brought to a pH of 6.2 with 1.0 M nitric acid. After vigorous mixing the white precipitate was collected

on a medium frit and was washed with water, alcohol, and ether. Drying the precipitate in a vacuum desiccator over phosphorus pentoxide for 3 days gave 26.0 g (87%) of (71) as a snow white solid.

The spectral data were as follows: IR (nujol mull and fluorolube mull) 2180 cm^{-1} on PE 137. No absorptions attributable to silver oxide or silver carbonate (1300-1500 cm^{-1}) were present.

7-Norbornadienylisocyanate (68). Over a period of several minutes 15.3 g (0.12 mol) of a solution of 7-chloro-norbornadiene (68) in approximately 60 ml of dry liquid sulfur dioxide was added to a mixture of 19.5 g (0.13 mol) of silver isocyanate and 150 ml of dry liquid sulfur dioxide. After the addition was complete the reaction mixture was allowed to reflux while stirring with a magnetic spin bar for 1.5 hours. During this time the system was kept under an inert atmosphere of argon and in complete darkness. After this time the reaction mixture was allowed to warm to room temperature by letting the sulfur dioxide evaporate. During the evaporation of the sulfur dioxide 200 ml of anhydrous ether was added. After this the reaction mixture was filtered through a medium frit containing a layer of filter aid. Removal of the solvent in vacuo (rotary evaporator) from the resulting ether solution gave 15.1 g (94%) of the isocyanate (68) as an orange oil. No attempt was made to purify this compound and it was used immediately as obtained.

The spectral data were as follows: NMR ($CDCl_3$) τ3.1-3.3 (m, 4H, olefinic), 6.2-6.5 (m, 3H, bridgehead and C-7); ir (neat) 2200 cm^{-1} on PE 137.

Methyl N-7-Norbornadienylcarbamate (69). A solution of 7-norbornadienylisocyanate (68) in 70 ml of pentane just prepared from 3.8 g (0.03 mol) of the chloride (50) was added to 50 ml of anhydrous methanol containing a few drops of acetic acid. This solution was then stirred with a magnetic spin bar under an inert atmosphere of nitrogen. After maintaining the reaction under the above conditions for 20 hours the resulting brown mixture was concentrated to a volume of approximately 5 ml *in vacuo* (rotary evaporator). The concentrate was dissolved in a minimum amount of ether and chromatographed on a short silica gel column using 20% v/v ether-pentane as an elutant. Collection of the first yellow band gave 1.3 g of a yellow solid on removal of solvent *via* rotary evaporator. Trituration of this material with pentane and concentration of the resulting clear, colorless pentane solution *via* rotary evaporator afforded 930 mg [19% based on the chloride (50)] of (69) as a white solid, mp 63.5-65.5°. An analytical sample was prepared for CHN analysis by sublimation at room temperature and a pressure of 5 microns.

The spectral data were as follows: NMR ($CDCl_3$) τ3.2-3.4 (m, 4H, olefinic), 4.2-5.0 (broad d, 1H, N-H), 5.7-6.1 (broad d, 1H, C-7), 6.4 (s, 3H, methyl), 6.4-6.6 (m, 2H, bridgehead); ir (nujol mull) 3440, 3405, 2920, 1740, 1375, 1350 1310, 1210, 1070, 1050, 780, 740 cm^{-1} on Beckman IR 10; ms m/e 165 (M+), 164, 150 (base), 134, 133, 132, 106, 91, 79, 78, 77.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.19; H, 6.74; N, 8.42.

p-Chlorobenzoyl Nitrite (73). This material was prepared using the method of Baigrie, Cadogan, Mitchell, Robertson, and Sharp.[63] The material was carefully weighed and dissolved in anhydrous ether in a volumetric flask immediately after preparation and stored at Dry Ice temperature. In this way the actual amount of solution needed for each reaction was easily calculated. The solution was allowed to warm to room temperature just before use. Best results were obtained if the material was made within a few days of its anticipated use in about the amount needed instead of trying to make large quantities of the material and store it over a long period of time since the material slowly decomposes.

Methyl N-Nitroso-N-7-norbornadienylcarbamate (64). A volume, in this case 42.0 ml, of p-chlorobenzoyl nitrite solution containing 1.0 equivalents of p-chlorobenzoyl nitrite (73) was added to a solution of 1.07 g (0.0065 mol) of methyl N-7-norbornadienylcarbamate (69) in 100 ml of anhydrous ether containing 5.2 g of freshly fused anhydrous sodium acetate. The p-chlorobenzoyl nitrite solution was at room temperature. The mixture was stirred with a magnetic spin bar between -40 and -55° under an argon atmosphere for 4.5 hours. The yellow reaction mixture was then poured into 200 ml of ice cold aqueous 5% sodium bicarbonate solution and 300 ml of ice cold ether. After mixing and

separation of layers the ether phase was washed twice with 200 ml portions of ice cold aqueous 5% sodium bicarbonate solution and then twice with 200 ml portions of ice cold water. Drying of the ether phase over anhydrous magnesium sulfate, filtration, and removal of the solvent in vacuo (rotary evaporator) gave an orange yellow oil. The orange yellow oil was then chromatographed on a specially prepared 1.5 x 35 cm silica gel column using wet 3% v/v ether-pentane. The column was prepared by making it up using 3% v/v ether-pentane which had been shaken in a separatory funnel with water. Ether-pentane prepared in this same manner was used for elution. The yellow band was collected. The yellow solution was dried over anhydrous magnesium sulfate, filtered, and the solvent evaporated in vacuo (rotary evaporator) to give 930 mg (79%) of (64) as a yellow orange oil.

The spectral data were as follows: NMR ($CDCl_3$) τ3.1-3.6 (m, 4H, olefinic), 6.0 (s, 3H, CH_3), 5.9-6.1 (m, 3H, bridgehead and C-7).

Bases Used in the Attempts to Generate 7-Norbornadienylidene (1) from Methyl N-Nitroso-N-7-norbornadienylcarbamate (64) and N-Nitroso-N-7-norbornadienylurea (65).

(A) Sodium Methoxide. This was obtained as a 25% solution in methanol from Aldrich (54.0 g sodium methoxide/216 g solution).

(B) Lithium Ethoxide. To 100 ml of absolute ethanol under an atmosphere of argon was added 3.5 g (0.5 mol) of freshly cut lithium ribbon. After the lithium dissolved the mixture was refluxed for 13.5 hours. Upon cooling the mixture

solidified into a single solid mass. The excess ethanol was taken off in vacuo at room temperature overnight. This afforded 28.4 g of a white solid. To titrate 0.1527 g of this solid to a phenolphthalein endpoint 2.52 milliequivalents of 0.1000 N hydrochloric acid were required. Calculations showed that 1.56 milliequivalents would be needed if the solid were lithium ethoxide-ethanol and 2.96 if it were lithium ethoxide.

(C) Lithium Methoxide. To 150 ml anhydrous methanol was added slowly 5.1 g (0.75 mol) of lithium ribbon. The reaction system was a 200 ml three neck round bottom flask fitted with an efficient reflux condenser and drying tube plus an argon inlet. After most of the lithium had reacted an additional 15 ml of methanol were added and the system was brought to reflux for 23 hours. After cooling to room temperature the excess methanol was distilled off in vacuo to give 26.6 g (93%) of the product as a white solid.

The spectral data were as follows: IR (nujol mull) 1150, 1050 cm^{-1}; (fluorolube mull) 2900, 2800, 2750, 2575, 1450 cm^{-1} on PE 137.

(D) Lithium Ethoxide-Ethanol. To 50 ml of absolute ethanol under nitrogen was added lithium metal until the lithium metal reacted slowly. More ethanol, approximately 25 ml, was then added and the mixture brought to reflux until all of the lithium had dissolved. This gave a white gelatinous precipitate which upon cooling with an ice water

bath crystallized in a form which could be filtered. Filtration, washing with a small portion of ethanol, and air drying gave a white solid.

The spectral data were as follows: IR (potassium bromide pellet) 3580, 3000, 1580, 1520, 1450, 1000, 860, 680, 640 cm^{-1} on Beckman IR 10.

Decomposition of Methyl N-Nitroso-N-7-norbornadienyl-carbamate (64) by Sodium Methoxide. In a typical reaction 0.295 g of a 25% sodium methoxide in methanol solution which had been diluted with 0.3 ml of anhydrous methanol was added dropwise over a six minute period to a solution of 102 mg (0.53 mmol) of methyl N-nitroso-N-7-norbornadienyl-carbamate (64) in 100 ml of anhydrous ether. The reaction solution was held at reflux while stirring with a high speed mechanical stirrer in a Mortan flask under an argon atmosphere. After the addition was complete the reaction solution was allowed to stir under the above conditions for 24 minutes. The resulting brown orange solution was poured into a mixture of 300 ml of ice cold ether and 200 ml of ice cold water. After mixing and separation of phases the ether phase was washed twice with ice cold water. The ether phase was dryed over anhydrous magnesium sulfate, filtered, and the solvent evaporated *in vacuo* (rotary evaporator) to give 42.6 mg of a red brown oil. Analysis of the crude product *via* nmr, tlc, and glpc and attempts to isolate products by column chromatography gave no evidence for the presence of carbene products. Carrying the reaction out in the presence

of dimethylfumarate gave the Michael adduct of sodium methoxide and dimethylfumarate as the only isolatable product.

Decomposition of Methyl N-Nitroso-N-7-norbornadienyl-carbamate (64) by Lithium Ethoxide. By way of a solid addition tube was added 1.5 equivalents, as determined by titration, of lithium ethoxide in one lot to a solution of 101 mg (0.52) mmol) of methyl-N-nitroso-N-7-norbornadienyl-carbamate (64) in 100 ml of anhydrous ether. The mixture was stirred with a high speed mechanical stirrer in a Mortan flask under an argon atmosphere. The reaction was held at 0^{o} for 30 minutes after the addition and when no visual change took place it was warmed to room temperature for 4.25 hours. At the end of this time the resulting orangish brown mixture was poured into a mixture of ether and water. After mixing and separation of phases the ether phase was washed with two additional portions of water. Most of the color washed into the aqueous phases. The organic phase was dryed over anhydrous magnesium sulfate, filtered, and the solvent removed in vacuo (rotary evaporator) to give 64.1 mg of a orangish brown oil. Column chromatography of this oil on silica gel with 3% v/v ether-hexane afforded 22.2 mg (26%) of methyl 7-norbornadienylcarbonate (109) as a yellow oil.

The spectral data were as follows: NMR ($CDCl_3$) τ3.3-3.6 (m, 4H, olefinic), 5.5 (m, 1H, C-7), 6.3 (s, 3H, CH_3), 6.3-6.5 (m, 2H, bridgehead); ir ($CHCl_3$) 1730, 1250, 1050 cm^{-1} on Beckman IR 10; ms m/e 166 (M+), 122, 121, 107, 91 (base), 79, 78, 77, 59, 44.

7-Norbornadienylurea (70). Into 100 ml of a saturated benzene ammonia solution at room temperature was added 15.1 g (0.114 mol) of 7-norbornadienylisocyanate (68) dissolved in a small amount of benzene. An orangish precipitate formed almost immediately upon addition of the isocyanate (68) and the flask became rather warm. The reaction mixture was stirred with a magnetic spin bar while bubbling in ammonia for an additional 1.5 hours. The resulting precipitate was collected on a medium frit to give 10.3 g of a dark beige solid. A dark hard lump of material which seemed to form quickly just before the orangish precipitate began to form was kept separate from the product. Recrystallization of the beige solid from hot tetrahydrofuran afforded 4.4 g (26% based on (68)) of (70) as a beige solid. An analytical sample was prepared by recrystallizing from tetrahydrofuran three times to give a white solid, mp 175-184° d.

The spectral data were as follows: NMR (DMSO-d_6) τ3.1-3.4 (m, 4H, olefinic), 3.5-3.9 (broad d, 1H, N-H), 4.3-4.8 (broad s, 2H, NH_2), 5.8-6.2 (broad d, 1H, C-7), 6.4-6.7 (m, 2H, bridgehead); ir (potassium bromide pellet) 3450, 3310, 3210, 3100, 3000, 1660, 1600, 1570, 1550, 1540, 1395, 1330, 1315, 1240, 1210, 1170, 740, 650, 630 cm^{-1} on Beckman IR 10; ms m/e 150 (M+, weak), 149, 133, 132, 106 (base), 91, 79, 65.

Anal. Calcd for $C_8H_{10}N_2O$: C, 63.68; H, 6.71; N, 18.65. Found: C, 63.91; H, 6.73; N, 18.60.

N-Nitroso-N-7-norbornadienylurea (65). To a mixture of 2.1 g (0.014 mol) of 7-norbornadienylurea (70) and 11.5 g of freshly fused anhydrous sodium acetate in 100 ml of anhydrous ether stirred magnetically under argon at -45°, was added 1.0 equivalents of p-chlorobenzoyl nitrite solution at room temperature. The reaction was allowed to run under the above conditions for 4.5 hours. After this time the entire contents were poured into a mixture of 300 ml of ice cold ether and 200 ml of ice cold aqueous 10% sodium bicarbonate solution. After mixing and separation of layers the ether phase was washed twice more with 200 ml portions of ice cold aqueous 10% sodium bicarbonate solution and finally once with 200 ml of ice cold water. The ether phase was dried over anhydrous magnesium sulfate, filtered, and the solvent removed in vacuo (rotary evaporator) to afford 1.45 g of a yellow brown solid. Chromatography of the crude product on a silica gel column with 50% v/v ether-pentane gave on collection of the bright yellow band 944 mg (38%) of (65) as bright canary yellow needles. A small amount of material was rechromatographed to provide a sample with mp 99-101° d.

The spectral data were as follows: NMR ($CDCl_3$) τ3.1-3.5 (m, 2H, olefinic), 3.8 (very broad s, 2H, NH_2), 5.8-6.0 (m, 2H, bridgehead), 6.0-6.2 (m, 1H, C-7); ir (potassium bromide pellet) 3440, 3310, 3250, 3170, 3080, 3010, 2970, 1710, 1610, 1590, 1500, 1400, 1340, 1310, 1240, 1200, 980, 700 cm^{-1} on Beckman IR 10; ms m/e 179 (M+, very weak), 149, 132, 119, 91, 79, 77, 43 (base).

Typical Decomposition of N-Nitroso-N-7-norbornadienylurea (65) under Basic Conditions. In a typical reaction 18.9 mg of lithium methoxide was added as a solid in one batch to a stirred solution of 48.8 mg (0.27 mmol) of N-nitroso-N-7-norbornadienylurea (65) in 50 ml of anhydrous ether at 0°. The mixture was stirred at 0° for 5.5 hours. During this period the bright yellow color of the solution became dull although no bubbles or transient colors were observed. The reaction was worked up by diluting with 150 ml of ether and washing with three 150 ml portions of water. Drying over anhydrous magnesium sulfate and removal of solvent *in vacuo* (rotary evaporator) gave 28.6 mg of a brown oil. No carbene products could be detected by normal analysis methods. Other conditions attempted are recorded in Table 1. Under none of these conditions have any carbene products been detected.

Table 1. Decomposition of N-Nitroso-N-7-norbornadienylurea (65) Under Basic Conditions.

Base	Solvent	T (C°)	Trap
Lithium Ethoxide	Ether	RT	None
Lithium Methoxide	Ether	0	Dimethylfumarate
Lithium Methoxide	Ether	0	None
Lithium Methoxide	Pentane	0	None
Lithium Methoxide	Isobutylene	-7	Isobutylene
Sodium Methoxide	Isobutylene	-7	Isobutylene
Lithium Ethoxide-Ethanol	Isobutylene	-7	Isobutylene

Decomposition of N-Nitroso-N-7-norbornadienylurea (65) in Heptane at 90°. In a typical reaction 97.7 mg (0.55 mmol) of N-nitroso-N-7-norbornadienylurea (65) was added as a solid

in one batch to 10 ml of heptane which was stirred at 90° under an argon atmosphere. Gas evolution occurred immediately and was quite rapid. The gas evolution was complete within a few minutes and no transient colors were observed. Some brownish insoluble material formed and the appearance of the solution changed from bright yellow to dull yellow. The reaction solution was held at 90° for 4 minutes after the addition and was quenched by cooling with an ice water bath. Evaporation of the heptane to near dryness in vacuo (rotary evaporator) gave an undetermined amount of an orange oil containing some brown solid with the nmr spectrum shown in Figure 1. In another run a similar material was obtained with the nmr spectrum shown in Figure 2.

In another run methanol was added to the crude product mixture and the progress followed by nmr to give the spectrum shown in Figure 3.

Decomposition of N-Nitroso-N-7-norbornadienylurea (65) in Heptane in the Presence of Dimethylfumarate at 90°. As a solid in one batch 41.1 mg (0.23 mmol) of N-nitroso-N-7-norbornadienylurea (65) was added to a solution of 400 mg (12 fold excess) of dimethylfumarate in 10 ml of heptane. The solution was stirred with a magnetic spin bar at 90° under an argon atmosphere. Gas evolution was immediate and complete within 2 minutes. No transient colors were observed. After 2.5 minutes at 90° the reaction was cooled with an ice water bath. The excess dimethylfumarate which crystallized

upon cooling was filtered off and the solvent removed in vacuo (rotary evaporator) from the filtrate to give an undetermined amount of an orange oil and white solid. The nmr spectrum of this material is shown in Figure 4.

The crude product mixture was then unintentionally exposed to ethanol which resulted in the appearance of new signals in its nmr spectrum as shown in Figure 5. Most of the remaining dimethylfumarate was removed by sublimation. When an nmr of this material was obtained it resulted in the following spectrum shown in Figure 6. Chromatrography of this material on a silica gel column with 75% v/v ether-hexane gave 13.2 mg of an orange oil with the nmr spectrum shown in Figure 7.

Decomposition of N-Nitroso-N-7-norbornadienylurea (65) in Heptane in the Presence of Lithium Carbonate at 90°. To a stirred suspension of 52 mg (0.7 mmol, 5 fold excess) of lithium carbonate in 10 ml of heptane at 90° under argon was added as a solid in one batch 25.2 mg (0.14 mmol) N-nitroso-N-7-norbornadienylurea (65). Gas evolution was immediate and quite rapid but no transient colors were observed. The reaction mixture was held at 90° for an additional four minutes and then quenched by cooling with an ice water bath. The lithium carbonate was filtered off on a medium frit and the solvent removed in vacuo (rotary evaporator) to give an undetermined amount of an orangish oil. Spectral analysis by nmr showed the products to be the same as in experiments where no lithium carbonate had been used.

Decomposition of N-Nitroso-N-7-norbornadienylurea (65) in Triglyme at 200°. To 15 ml of triglyme which was stirred with a magnetic spin bar under an argon atmosphere at 200° was added dropwise over a 15 minute period a solution of 50.8 mg (0.28 mmol) of N-nitroso-N-7-norbornadienylurea (65) in 5 ml of triglyme. The color of the reaction solution changed from colorless to yellow to a bright brown as the reaction progressed. The reaction was cooled with an ice water bath after heating at 200° for five minutes. After diluting with 400 ml of pentane the solution was washed with ten 50 ml portions of water to remove the triglyme. Drying of the pentane solution over anhydrous magnesium sulfate and removal of the solvent in vacuo (rotary evaporator) afforded an undetermined amount of an orange brown oil. Spectral analysis by nmr and gc-ms showed only a trivial product tentatively identified as dimethoxybenzene. This material was trivial since a material with the same spectral properties was independently found to be a contaminant in the triglyme.

Experimental Method for Thermolysis of N-Nitroso-N-7-norbornadienylurea (65) in a Hot Tube. The experimental system as shown in Figure 8 consisted of an open tube inclined at approximately 45°. At the head of the tube, which was at an angle of 45° to the inclined portion, was a solid addition tube containing the substrate and downstream from it a nitrogen inlet. The inclined portion of the tube was heated by a heating tape and the temperature monitored

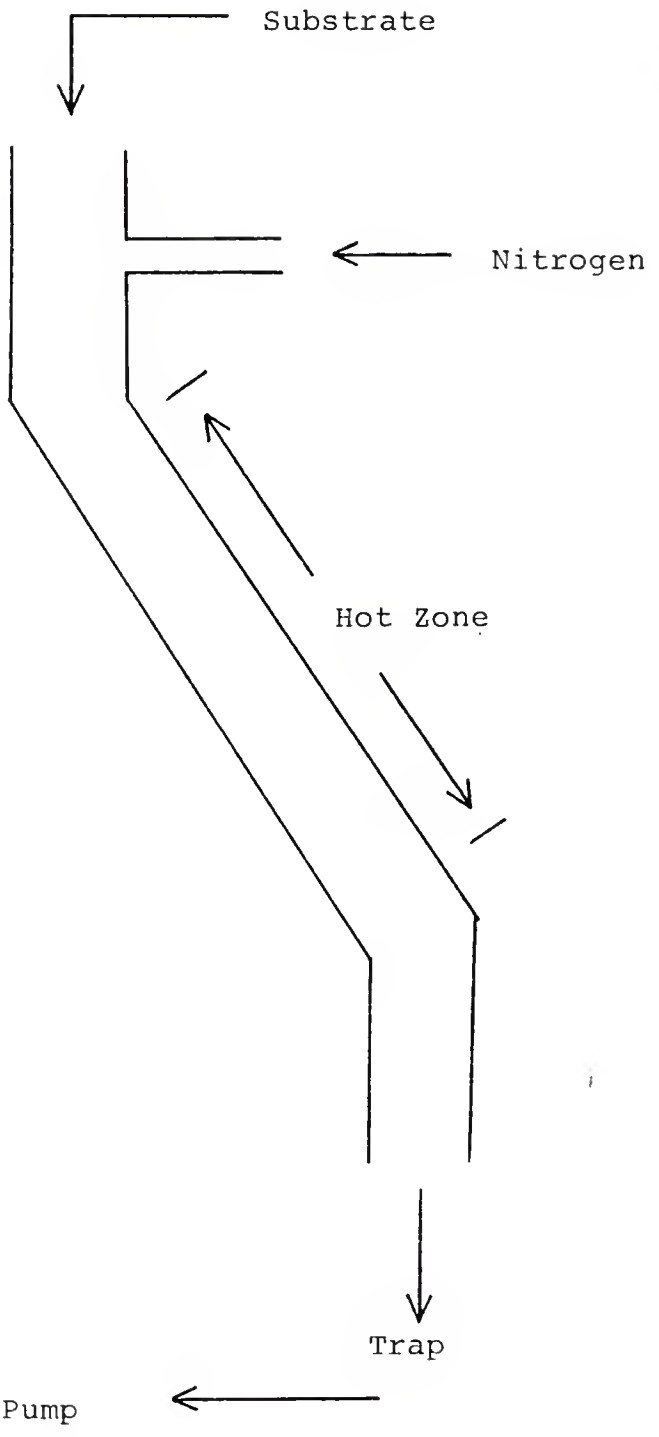


Figure 8

by an external thermocouple. Products were trapped by a liquid nitrogen trap at the end of this tube. A plug of glass wool was placed in the head of the trap and cooled with liquid nitrogen to help break up any aerosoling. Pressure and nitrogen flow were regulated by evacuating the system to approximately 20 microns and then adjusting the nitrogen flow so as to achieve the final desired pressure. The substrate was added to the hot tube slowly over a 10 to 15 minute period. Nonvolatile and volatile products were worked up separately by allowing the volatiles to distill into the bottom of the trap and then dissolving them in chloroform-d for direct spectral analysis by nmr. Nonvolatiles which remained at the top of the trap and in the cool portions of the tube before the trap were collected by washing them out with methylene chloride. Removal of the methylene chloride in vacuo (rotary evaporator) afforded the nonvolatile products which were analyzed by their nmr and uv spectra.

Yields of products were obtained by addition of a known amount of cyclooctane to the nmr sample and integration of peaks. In several runs yields of heptafulvalene (14) were also obtained from its ultraviolet spectra. The yield of benzene (22) in one instance was determined by gas chromatography. Identification of (14) was done by comparison of its nmr spectrum with that of an authentic sample and by tlc by comparing its R_f value with that of an authentic sample. Toluene (23) and (22) were identified by comparison of their

nmr spectra with those of authentic samples. In addition (22) was also identified in one instance by gc-ms. The isomeric dimers (18) and (19) were identified by comparison of their very characteristic nmr spectra with those published in the literature[26] and from their mass spectra.

Typical Thermolysis of N-Nitroso-N-7-norbornadienylurea (65) in a Hot Tube at 300°. In a typical experiment 47.1 mg (0.263 mmol) of N-nitroso-N-7-norbornadienylurea (65) was exposed to the hot tube with the temperature set at 300° and a pressure of 3 torr. The products were worked up and analyzed in the manner described in the experimental method. A brown material was found in the cool part of the tube before the trap and in the top of the trap. A yellow liquid which partially solidified on warming to room temperature to give a white solid and a yellow liquid was found in the bottom of the trap. The products had a rather strong odor. The analysis showed the presence of the two isomeric dimers (18) and (19) in an 11% yield and heptafulvalene (14) in a 9% yield as nonvolatiles. The volatile portion consisted of benzene (22) in a 3% yield. In addition some material(s) with a complex nmr resonance from τ2.4 to 3.0 was/were a part of the nonvolatiles.

Typical Thermolysis of N-Nitroso-N-7-norbornadienylurea (65) in a Hot Tube at 400°. In a typical experiment 43.4 mg (0.242 mmol) of N-nitroso-N-7-norbornadienylurea (65) was exposed to the hot tube with the temperature set at 400° and a pressure of 3 torr. The products were worked up and

analyzed in the manner described in the experimental method. A brown oil was found in the cool part of the tube before the trap and in the top of the trap. A yellow liquid which partially solidified on warming to room temperature to give a white solid and a yellow liquid was found in the bottom of the trap. The products had a rather strong odor. The volatile portion consisted of benzene (22) in a 13% yield. The nonvolatile portion consisted of an undetermined amount of materials which have been identified as aromatic hydrocarbons.

The spectral data were as follows: NMR ($CDCl_3$) τ2.4-3.0 complex pattern; gc-ms (5' x 1/4" 3% SP 2100 column, 200°) m/e 154 (base), 153, 152, 77, 76; 182, 91 (base); 180, 179 (base), 178, 165, 89, 76; 180 (base), 179, 178, 165, 89, 88. The mass spectral data given here are only a representative sample of the gc-ms data obtained. Tentative assignments for the portion of the data given here are biphenyl, bibenzyl, and two materials with molecular formulae of $C_{14}H_{12}$ respectively. The results from the other thermolysis experiments are shown in Table 2.

Table 2. Thermolysis of N-Nitroso-N-7-norbornadienylurea (65) in a Hot Tube.

T(°C)	Run	(18) + (19)	(14)	(22)	(23)
200	A	61	0	19[a]	___[b]
	B	13	0	0.5	0
250	A	34	0	18	4
	B	14	5	2	0
300	A	14	15-20	___[c]	___[c]
	B	13	7	4	0
	C	9	3[d]	4	0
	D	11	9[e]	3	0
	E	12	6[f]	trace	0
350	A	0	38	11	0
	B	0	18	1	0
400	A	0	0	13	0
	B	0	0	3	0
	C	0	0	3	0

[a]The yield of (22) in this instance was determined by gc and its identity was determined from its mass spectrum. [b]The presence of (23) as a product at 200° was established from nmr spectra in earlier runs where no yields were obtained. In this run the volatiles were not analyzed by nmr and the amount of (23) was too low to be detected by gc. [c]The volatile products were not worked up separately in this run. [d]The yield was 3% by UV analysis. [e]The yield was 6% by UV analysis. [f]The yield was 4% by UV analysis.

Thermolysis of N-Nitroso-N-7-norbornadienylurea (65) in a Hot Tube at 400° and Trapping with Tetracyanoethylene (TCNE). In this experiment 70.0 mg (0.391 mmol) of N-nitroso-N-7-norbornadienylurea (65) were pyrolyzed in the hot tube at 400° and 3 torr. The volatile products were allowed to distill at -35° and 20 microns into a flask containing a dilute solution of tetracyanoethylene (TCNE) in tetrahydrofuran. The contents of the flask were then brought to atmospheric pressure and allowed to react at -30° for 30 minutes. When the solvent was removed *in vacuo* (rotary evaporator) a small amount of a brown solid was obtained.

Analysis by nmr showed weak signals corresponding to those published for 5,5,6,6-tetracyano-7-vinylidenebicyclo[2.2.1]-hept-2-ene (114).[6]

The spectral data were as follows: NMR (acetone-d_6) weak signals corresponding to the literature values for (114). The literature spectral data were as follows: NMR (acetone-d_6) τ3.1 (2H, t), 4.6 (2H, s), 5.15 (2H, t).[6]

Sodium Salt of Benzaldehyde Tosylhydrazone (113). This material was prepared by the method of R. C. Joines, A. B. Turner, and W. M. Jones.[4]

Thermolysis of the Sodium Salt of Benzaldehyde Tosylhydrazone (113) in a Hot Tube at 400°. Exposure of 54 mg (0.18 mmol) of the sodium salt of benzaldehyde tosylhydrazone (113) to the hot tube at a temperature of 400° and a pressure of 3 torr resulted in the formation of a brown solid on the cool parts of the pyrolysis tube and in the upper parts of the trap. Workup, as described in the experimental method, gave heptafulvalene (14) in a 33% yield.

Heptafulvalene (14). Authentic heptafulvalene (14) was prepared in the manner used by W. M. Jones and C. L. Ennis.[50]

Thermolysis of Heptafulvalene (14) in a Hot Tube at 400°. Addition of 39.7 mg (0.22 mmol) of heptafulvalene (14) to the hot tube at a temperature of 400° and a pressure of 3 torr resulted in a dark solid being deposited on the cooler parts of the pyrolysis tube and the upper parts of the trap. Workup, as described in the experimental method, gave heptafulvalene (14) in a 32% recovery.

Isolation and Identification of syn- and anti-Pentacyclo-[10.2.0.$0^{4,12}$.$0^{5,11}$.$0^{8,11}$]tetradeca-2,6,9,13-tetraene (18) and (19). Samples of (18) and (19) obtained from a series of runs were combined. Chromatography of these materials on a short silica gel column with pentane gave a material that was predominately (18) and (19) except for some unidentified aromatic materials and silicone grease. A substantial amount of the silicone grease was removed by trituration with acetone.

The spectral data were as follows: NMR (100 MHz, $CDCl_3$) see Figure 9; ms m/e 180 (M+), 179, 178 (base), 165. The literature spectral data were as follows:[26] NMR[75] dimer A, τ3.7-3.9 (4H, AB, J = 1.3 Hz, cyclobutenes), 4.2 (4H, s, cyclopentenes), 6.45 (2H, m, methines), 7.35 (2H, m, methines); dimer B, τ3.8 (4H, s, cyclobutenes), 4.2-4.4 (4H, AB, J=2.9Hz, cyclopentenes), 6.4 (2H, m, methines), 6.7 (2H, m, methines); ms m/e 180.

Thermolysis of syn- and anti-Pentacyclo[10.2.0.$0^{4,12}$.$0^{5,11}$.$0^{8,11}$]tetradeca-2,6,9,13-tetraene (18) and (19) in a Hot Tube at 350°. The mixture of dimers (18) and (19) isolated in the preceeding section was coated in its entirety on glass beads with a mesh size of 60-80 and pyrolyzed in the hot tube at 350°. In a previous run the N-nitroso urea (65) coated on the same type beads under the conditions used here gave a 13% yield of heptafulvalene (14). Workup as described in the experimental method followed by nmr analysis did not reveal any (14) as a product.

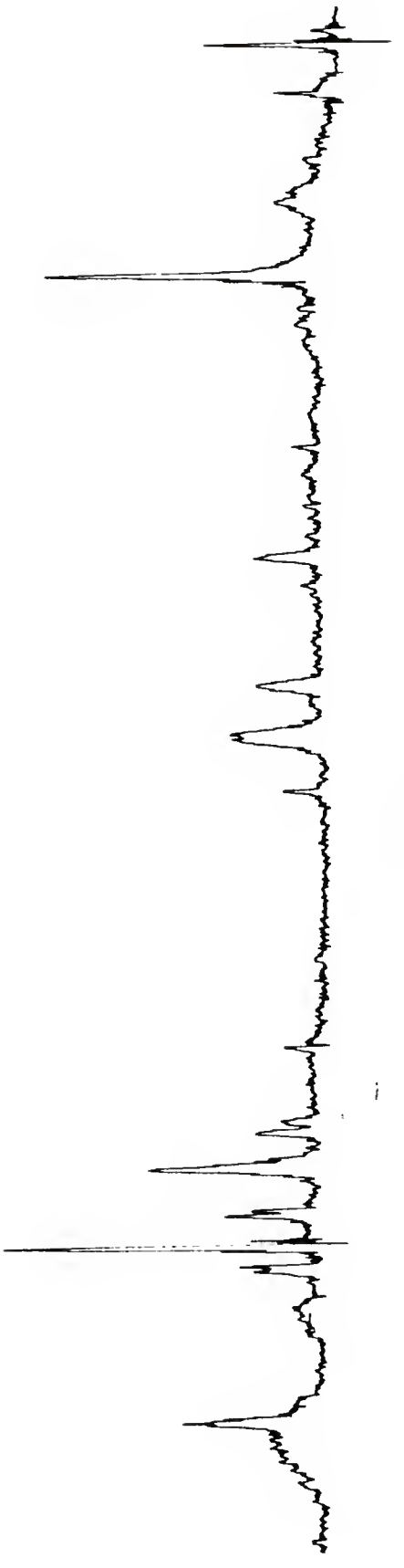
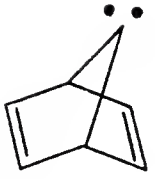
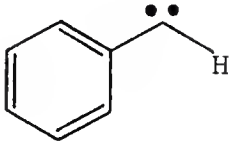
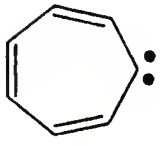


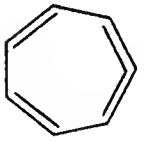
Figure 9

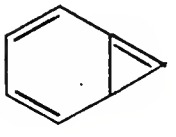
APPENDIX

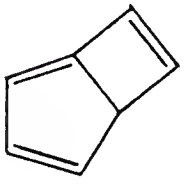
(1) 

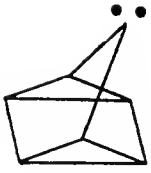
(2) 

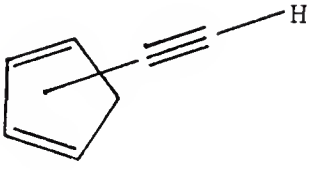
(3) 

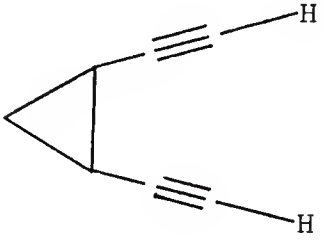
(4) 

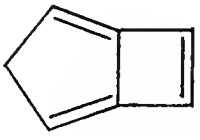
(5) 

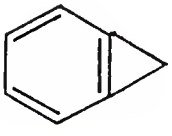
(6) 

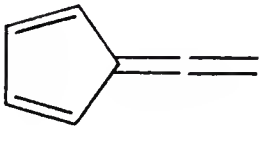
(7) 

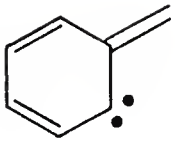
(8) 

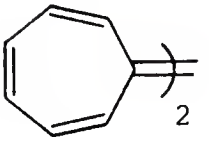
(9) 

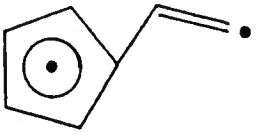
(10) 

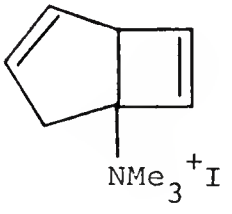
(11) 

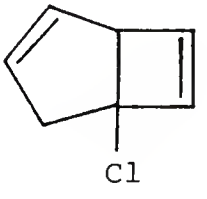
(12) 

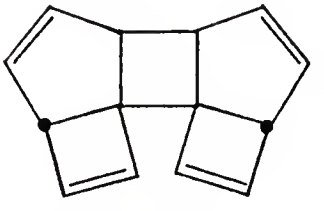
(13) 

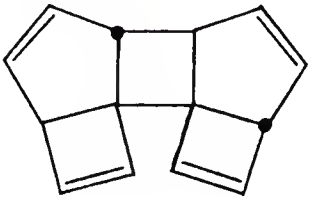
(14) 

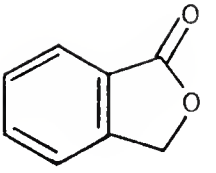
(15) 

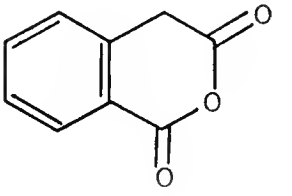
(16) 

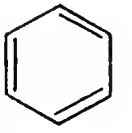
(17) 

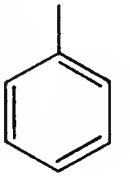
(18) 

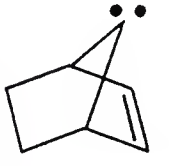
(19) 

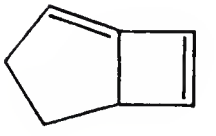
(20) 

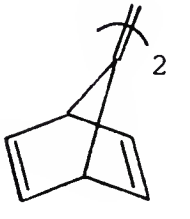
(21) 

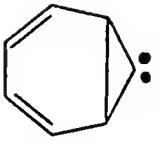
(22) 

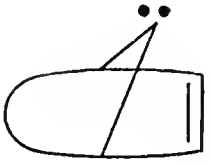
(23) 

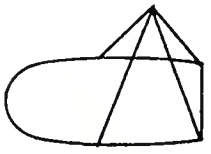
(24) 

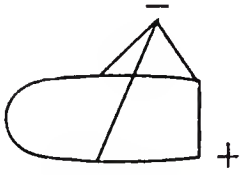
(25) 

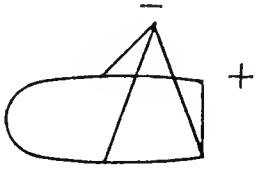
(26) 

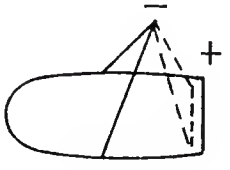
(27) 

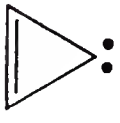
(28) 

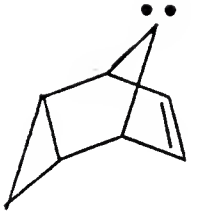
(29) 

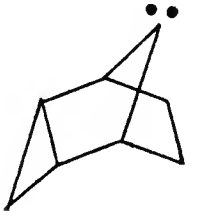
(30) 

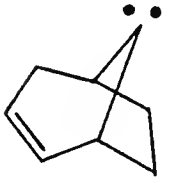
(31) 

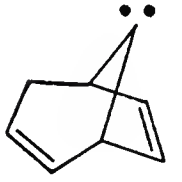
(32) 

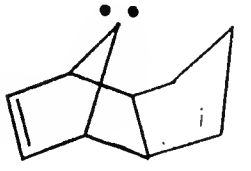
(33) 

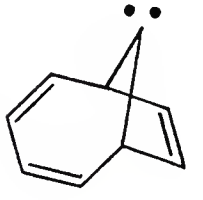
(34) 

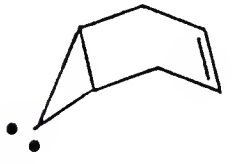
(35) 

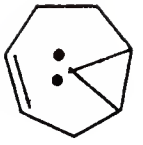
(36) 

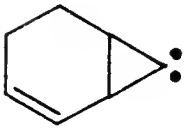
(37) 

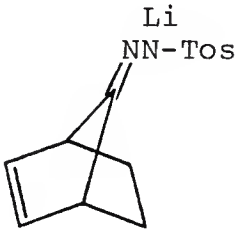
(38) 

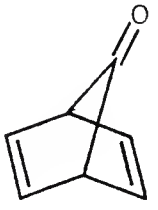
(39) 

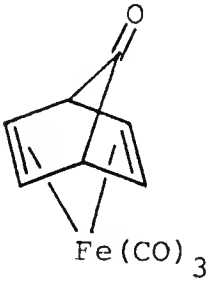
(40) 

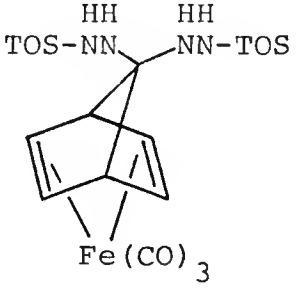
(41) 

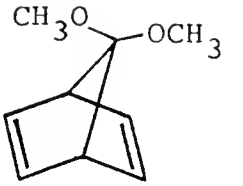
(42) 

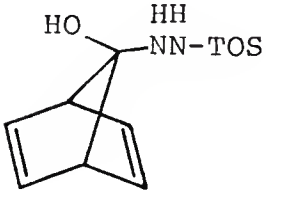
(43) 

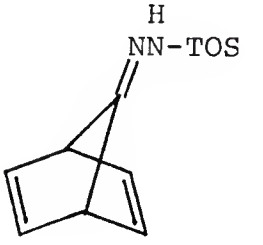
(44) 

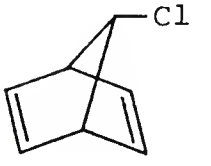
(45) 

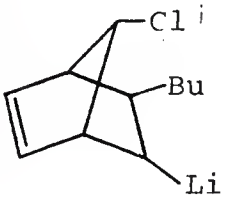
(46) 

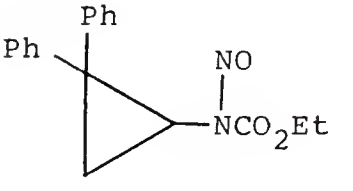
(47) 

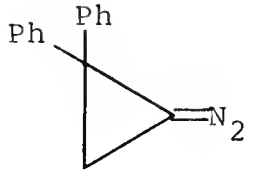
(48) 

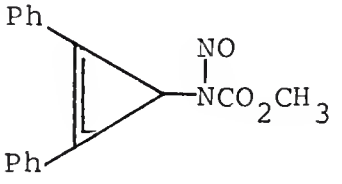
(49) 

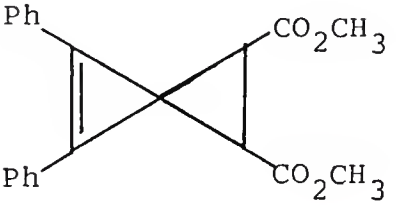
(50) 

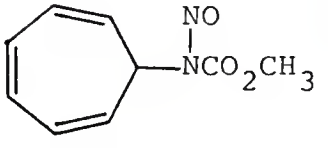
(51) 

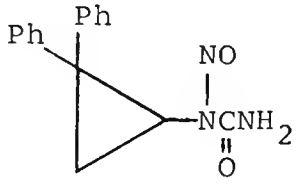
(52) 

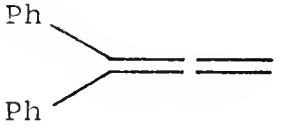
(53) 

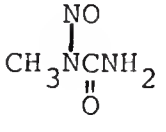
(54) 

(55) 

(56) 

(57) 

(58) 

(59) 

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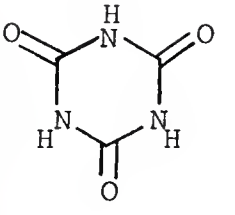
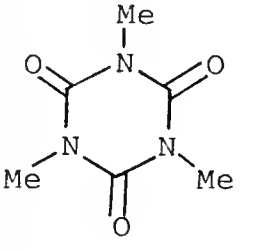
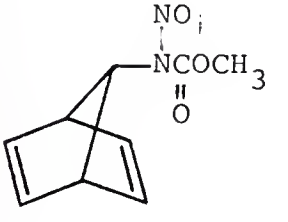
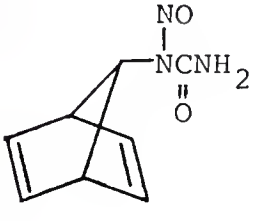
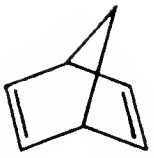
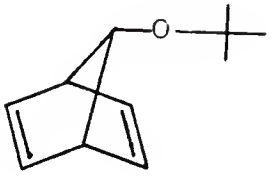
(62) 

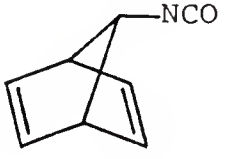
(63) 

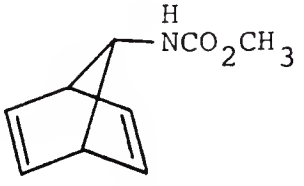
(64) 

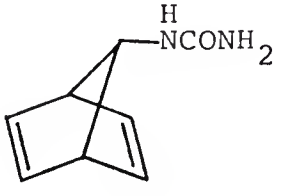
(65) 

(66) 

(67) 

(68) 

(69) 

(70) 

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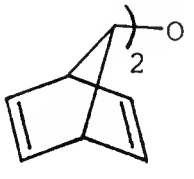
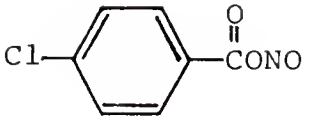
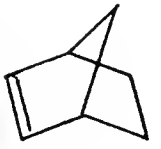
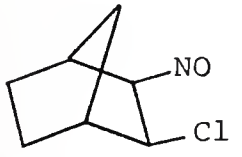
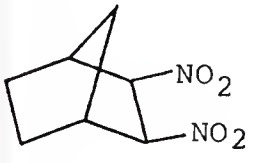
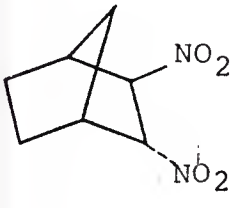
(72) 

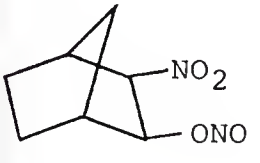
(73) 

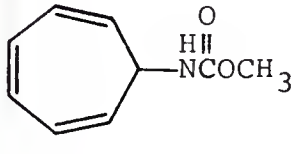
(74) 

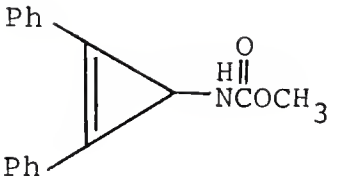
(75) 

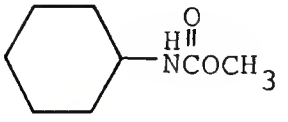
(76) 

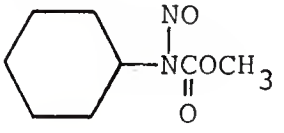
(77) 

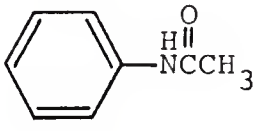
(78) 

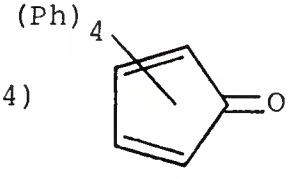
(79) 

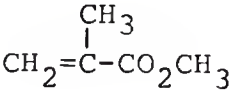
(80) 

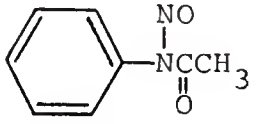
(81) 

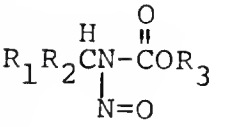
(82) 

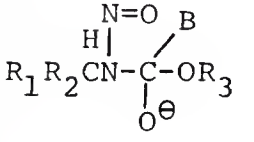
(83) 

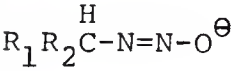
(84) 

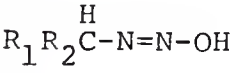
(85) 

(86) 

(87) 

(88) 

(89) 

(90) 

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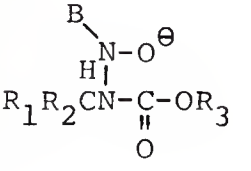
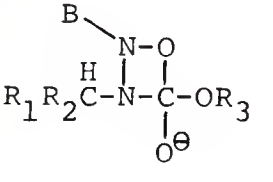
(92) 

(93) 

(94) B^-

(95) $R_3OCO_2^-$

(96)

(97)

(98)

(99) BH

(100)

(101)

(102)

(103)

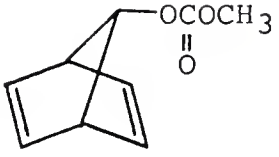
(104)

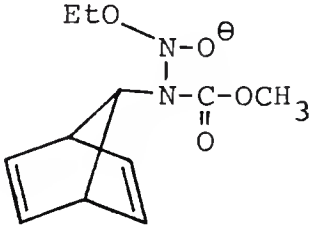
(105)

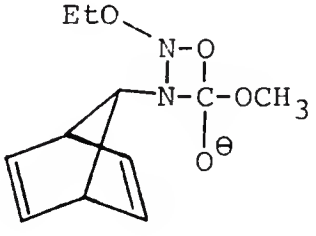
(106)

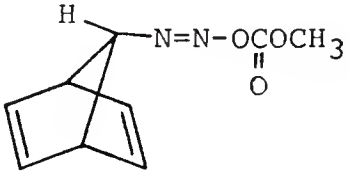
(107)

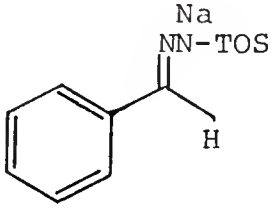
(108) OH^-

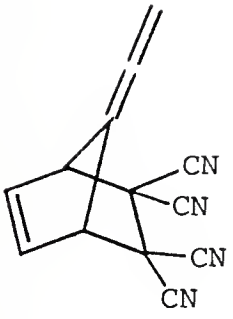
(109) 

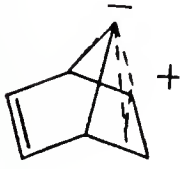
(110) 

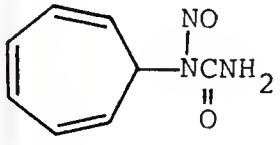
(111) 

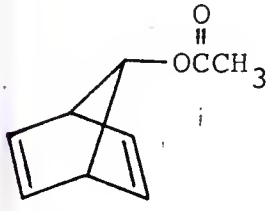
(112) 

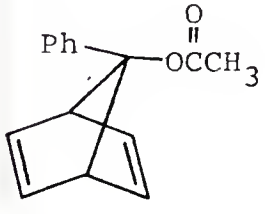
(113) 

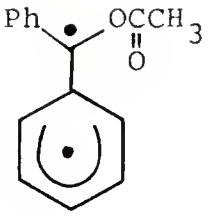
(114) 

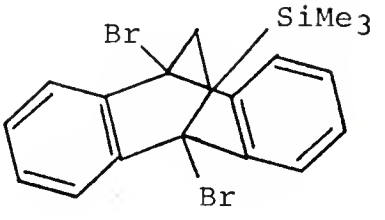
(115) 

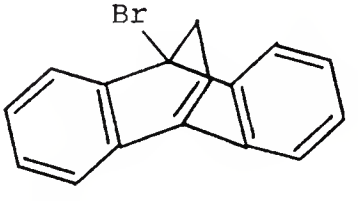
(116) 

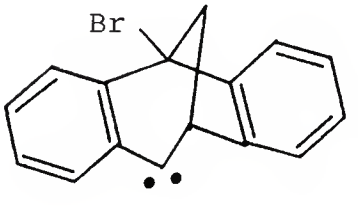
(117) 

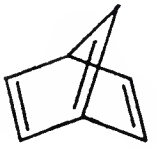
(118) 

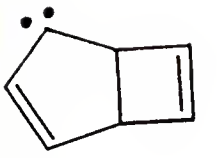
(119) 

(120) 

(121) 

(122) 

(123) 

(124) 

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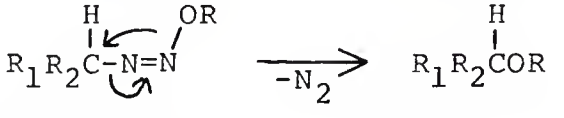

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BIOGRAPHICAL SKETCH

William Brown grew up in Inman, a small town in South Carolina. During high school he was a member of the Beta Club and played in the high school band.

He received his undergraduate training at Furman University in Greenville, South Carolina, from which he graduated magna cum laude in 1972 with a B.S. in chemistry. In addition he received a commission in the army reserve and is now a first lieutenant in the reserves. During his stay at Furman he was a member of the Furman Band, Phi Mu Alpha Sinfonia Fraternity, Chi Beta Phi Scientific Fraternity, and the National Society of Scabbard and Blade. He also participated in the Undergraduate Research Progam at Furman one summer.

Since coming to the University of Florida in 1972 he has worked under the direction of Professor William M. Jones. Upon completion of his doctoral work in organic chemistry he will be going to work for the Tennessee Eastman Company in Kingsport, Tennessee, as a chemist in their acid development department.

His primary interests are music, sports, and flying gliders.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William M. Jones, Chairman
Professor of Chemistry

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William R. Dolbier
Professor of Chemistry

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George B. Butler
Professor of Chemistry

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Gerhard M. Schmid
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 1978

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